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TP-FY99-0107

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MEMORANDUM FOR PRR (In-House Publication)

24 May 1999

FROM: PROI (TI) (STINFO)

SUBJECT: Authorization for Release of Technical Information, Control Number: AFRL-PR-ED-TP-FY99-0107
Bill Larson, "Identification and Condensation of Cyclic C₆ and Cyclic C₈ in Solid Argon and Matrix-Isolated
Boron/Carbon"

(Public Release)

Presentation

**Identification and condensation of cyclic C₆ and cyclic C₈
in solid argon**

**Characterization of matrix isolated B_JC_{n-J} J=0, 1, 2; n=3-11
in solid argon**

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HEDM RESEARCH GROUP

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**University of Florida
Department of Chemistry
Gainesville, Florida
June 8, 1999**

20021121 036

Rocket Science

$$\frac{m_{final}}{m_{initial}} = \exp - \frac{\Delta V}{g I_{sp}}$$

$$I_{sp} = \frac{1}{g} \sqrt{2(h_{propellant} - h_{exit})}$$

h = enthalpy per unit mass

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*Is there a point
to this chart?
a relationship
between 1st & 2nd
of that is relevant?*

SSME



Rockwell International

Rocketdyne Division

SPACE SHUTTLE MAIN ENGINE

The Space Shuttle Main Engine (SSME) was developed expressly for use on America's Space Shuttle. Using a mixture of liquid oxygen and liquid hydrogen, the SSME can attain a maximum thrust level (in vacuum) of 512,300 pounds at 109% power level. The regeneratively cooled engine also features high performance turbopumps for propellant and oxidizer that develop 77,310 horsepower and 29,430 horsepower, respectively. Ultra-high-pressure operation of the pumps and combustion chamber allows expansion of all hot gases through a high-area-ratio exhaust nozzle to achieve efficiencies never previously attained in a production rocket engine. These advantages allow a heavier payload to be carried without increasing launch vehicle size.

SPACE SHUTTLE MAIN ENGINE PERFORMANCE (FULL POWER LEVEL)



Maximum Thrust: (109% Power Level)

At Sea Level..... 408,750 pounds
In Vacuum..... 512,300 pounds

Throttle Range..... 65% - 109%

Pressures:

Hydrogen Pump Discharge..... 7.040 psia

Oxygen Pump Discharge..... 8.070 psia

Chamber Pressure..... 3.260 psia

Specific Impulse (In Vacuum)..... 453.5 seconds

Power: 5.07 GW (Exhaust, in Vacuum)

High Pressure Pumps

Hydrogen..... 77,310 horsepower

Oxygen..... 29,430 horsepower

Area Ratio..... 77.5:1

Weight: 6,367 kg/w..... 6,990 pounds

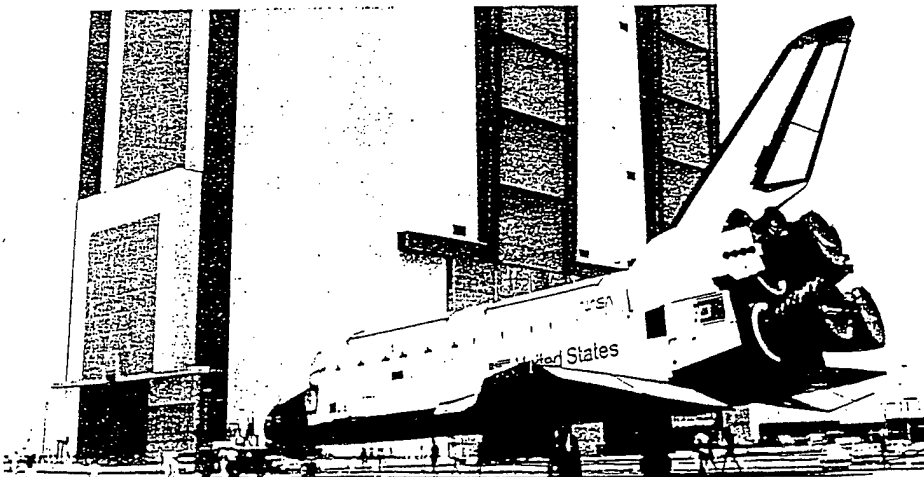
Mixture Ratio (O/F)..... 6.0:1

Dimensions: 168 in. long/96 in. wide

Propellants:

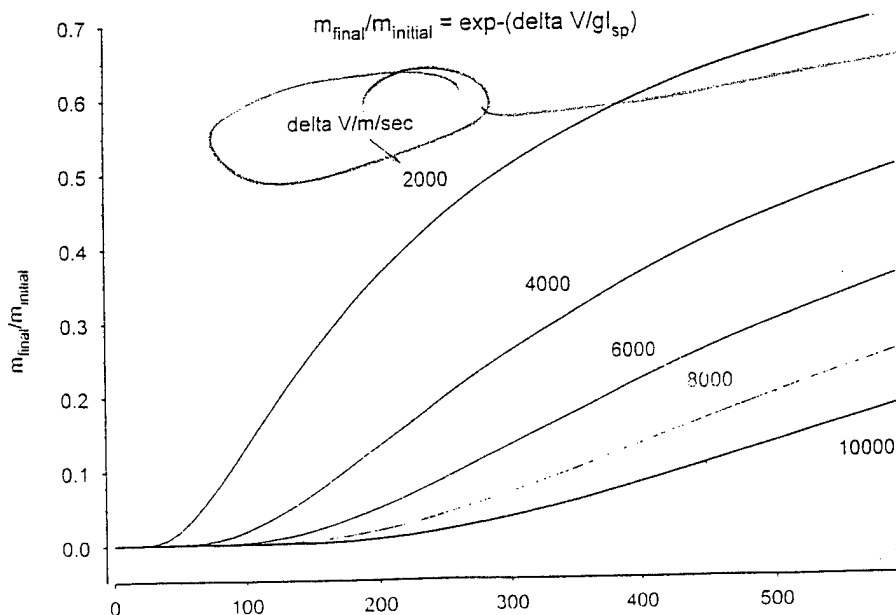
Fuel..... Liquid Hydrogen

Oxidizer..... Liquid Oxygen

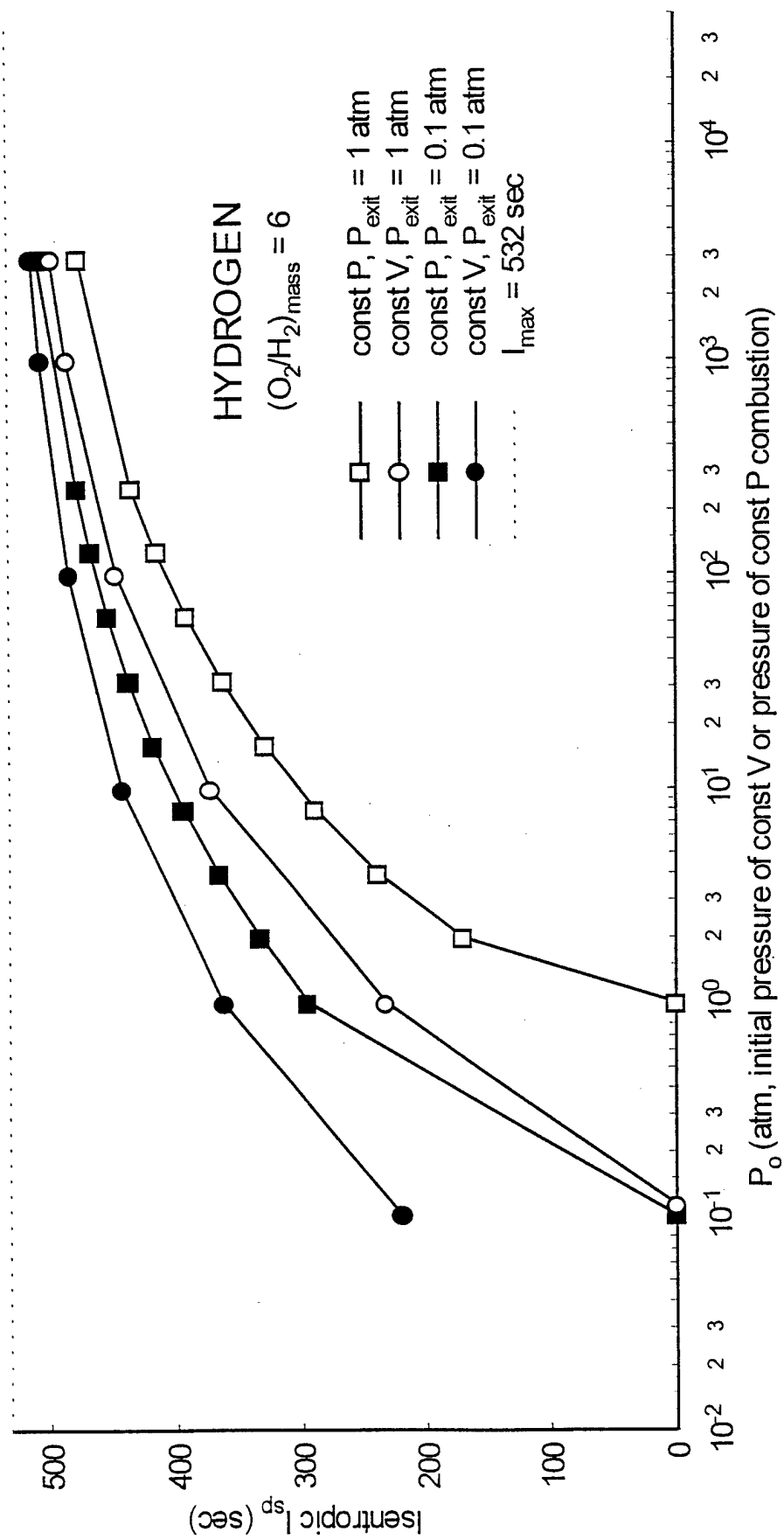


For more information contact: ELV Propulsion/Rockwell International/Rocketdyne Division/6633 Canoga Ave./
Canoga Park/CA/91303/(818)700-6027

Pub. 571-M-80b New 1-7



units?



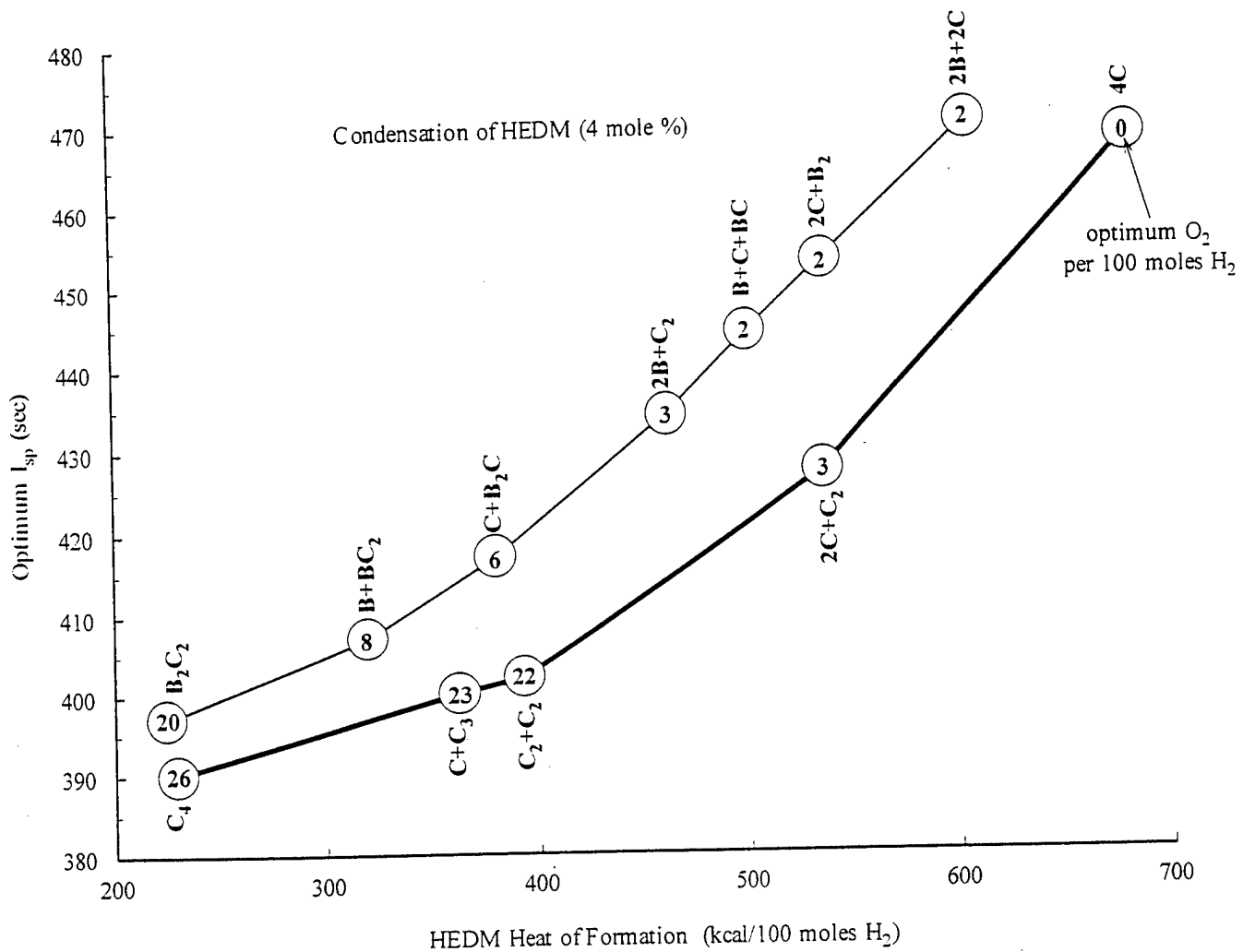


Figure 1. Specific impulse of HEDM containing 4 mole percent equivalent atom density in solid hydrogen with various stages of condensation. Numbers inside circles denote the optimum moles of O_2 per 100 moles of H_2 that produces the maximum I_{sp} for the indicated compositions. The calculations are based on the standard rocket operating conditions, 1000 psi combustion pressure and 1 atm nozzle exit pressure, which produce 389 sec with liquid oxygen/liquid hydrogen propellant. The propellant composed of 4 mole percent C-atoms produces maximum I_{sp} with no oxygen. If the atoms condense to 1 mole percent C_4 , the I_{sp} drops to the baseline 389 sec value.

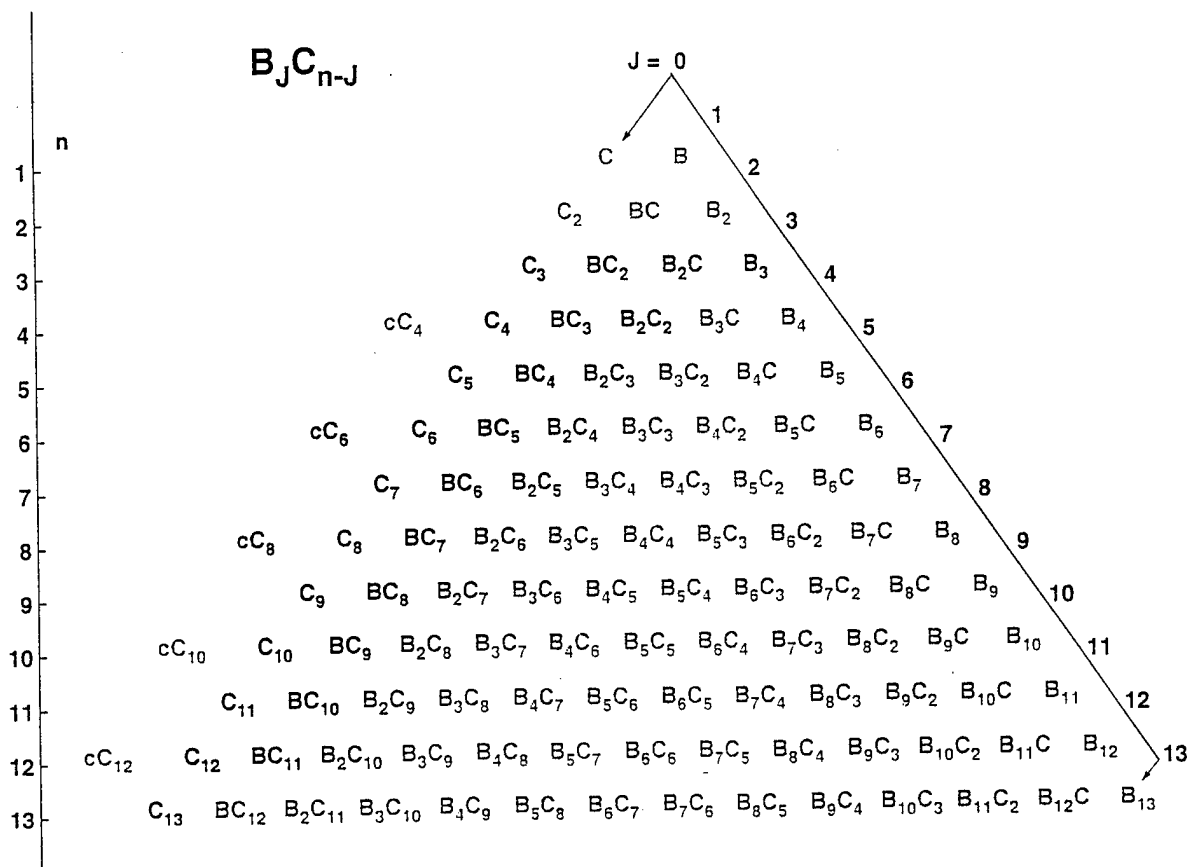
Objective - 5% atoms in cryogenic matrix

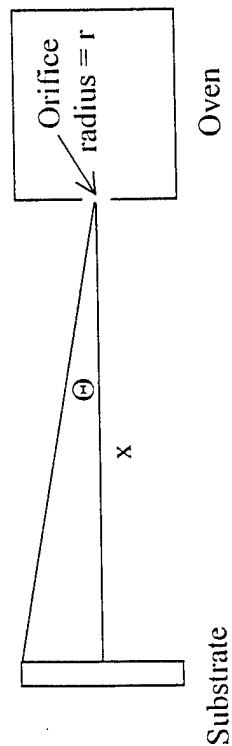
Approach

1. FTIR spectroscopy of $B_J C_{n-J}$ clusters isolated in 10 K argon matrix
2. Ab-initio calculations of cluster
 - (a) normal mode frequencies and frequency shifts of their isotopomers
 - (b) infrared absorption intensities (km mol^{-1})
3. Measurement of cluster distributions produced upon deposition and after annealing). Absolute column densities (molecules cm^{-2}) from Beer's Law

$$\langle \rho_i l \rangle = \frac{A_{\text{exp}}}{I_{\text{theory}}} N$$

$$A_{\text{exp}} = - \int_{\nu} \ln \left[\frac{E_t(\nu)}{E_0(\nu)} \right] d\nu$$



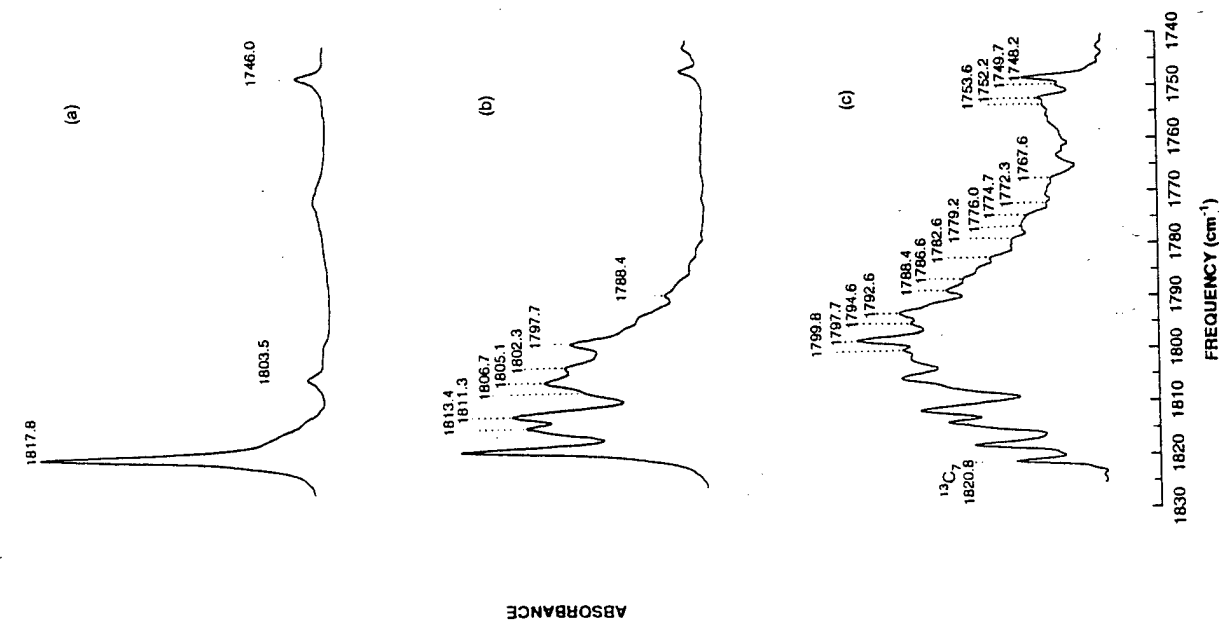
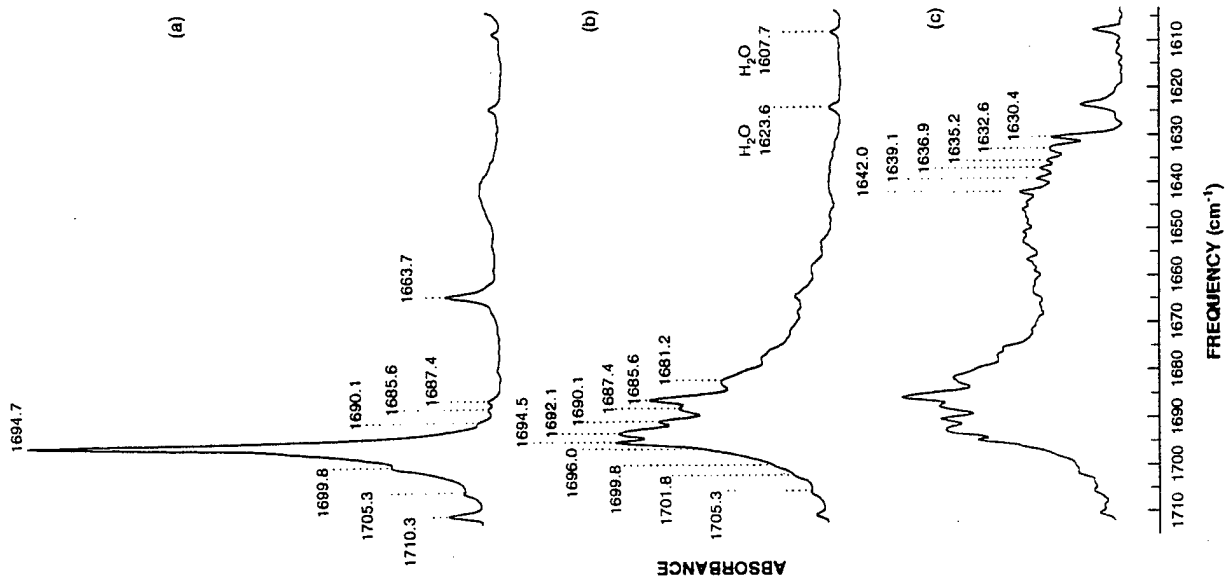


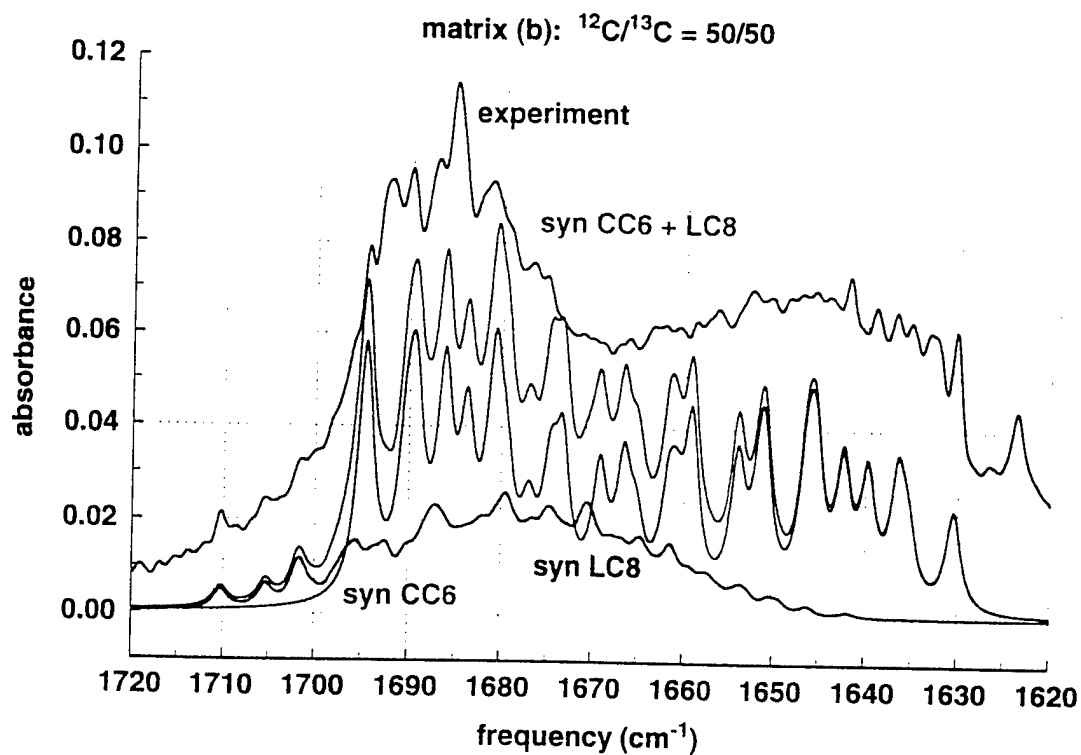
$$(1) \quad Q_{\text{atom}}(\Theta, x) = \frac{1}{4} \rho \bar{c} a \frac{\cos^3 \Theta}{\pi x^2} \quad (2) \quad Q_{\text{rad}}(\Theta, x) = \sigma T^4 a \frac{\cos^3 \Theta}{\pi x^2}$$

Table I. Properties of a boron evaporation oven^(a), $r = 0.05 \text{ cm}$, $\theta = 0$

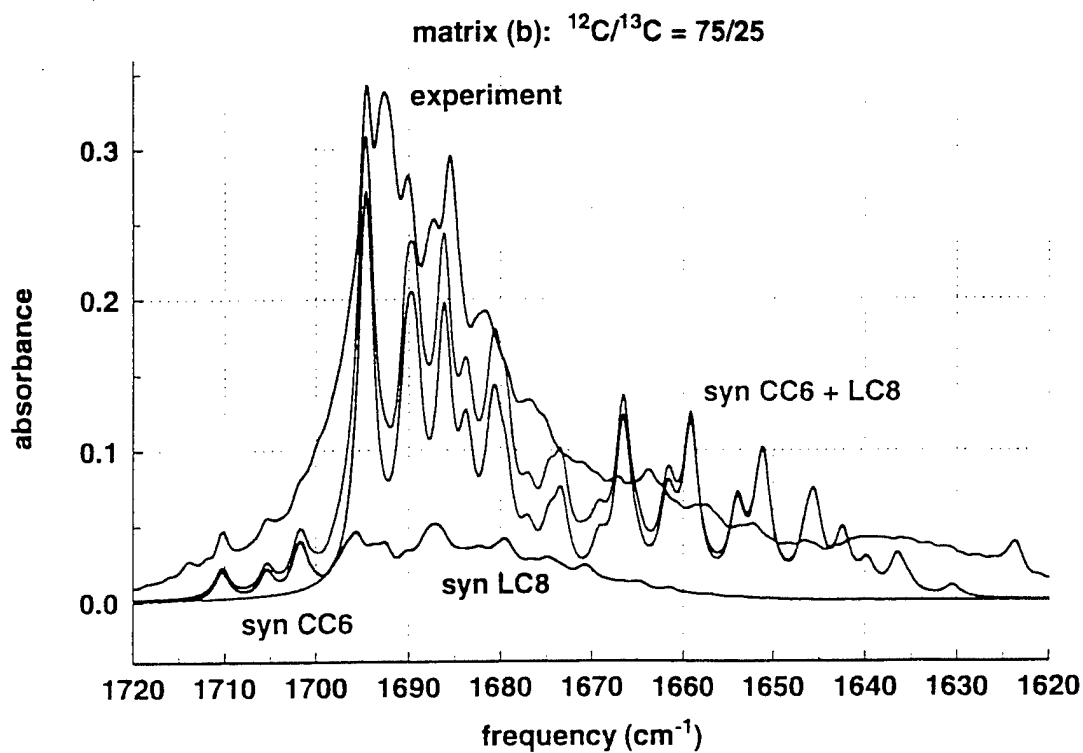
	$x = 10 \text{ cm}$		$x = 20 \text{ cm}$
P (Torr)	0.01	0.1	1
T (K)	2409	2631	2898
ρ ($\text{\#}/\text{cm}^3$)	4.01×10^{13}	3.67×10^{14}	3.33×10^{15}
\bar{c} (cm/s)	2.13×10^5	2.24×10^5	2.35×10^5
Evap rate ($\text{\#}/\text{s}$)	1.68×10^{16}	1.61×10^{17}	1.53×10^{18}
Evap rate (mg/hour)	1.11	10.6	101
λ (cm) ^(b)	100.0	10.9	1.20
$\text{Kn} = \lambda/2r$	1000	109	12.0
Q_{atom} ($\text{\#}/\text{cm}^2 \text{ s}$)	5.37×10^{13}	5.13×10^{14}	4.89×10^{15}
Q_{rad} (mW/cm ²)	4.74	6.75	9.93
			1.17×10^{16}
			3.78

(a) Based on vapor pressure data from Nesmeyanov's (1963) compilation, "Vapor Pressure of the Elements."
(b) Mean free path based on a collision diameter of $1.59 \times 10^{-8} \text{ cm}$ for boron + boron [Moelwyn-Hughes (1961), p25].

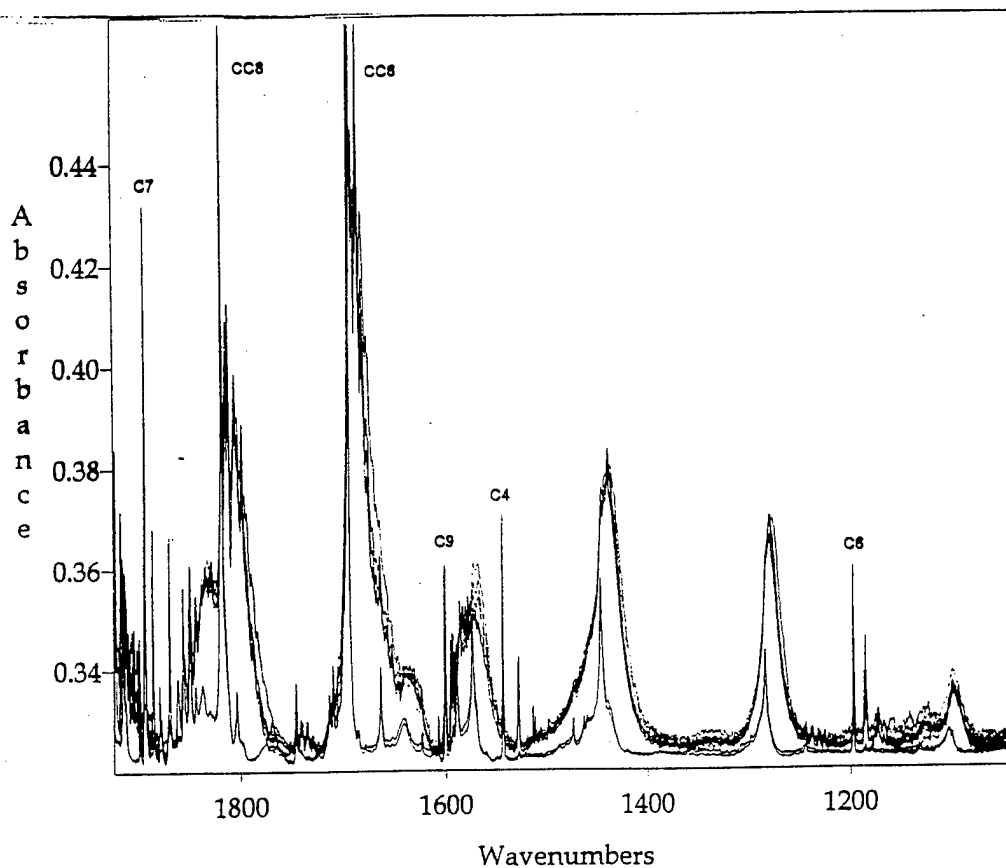
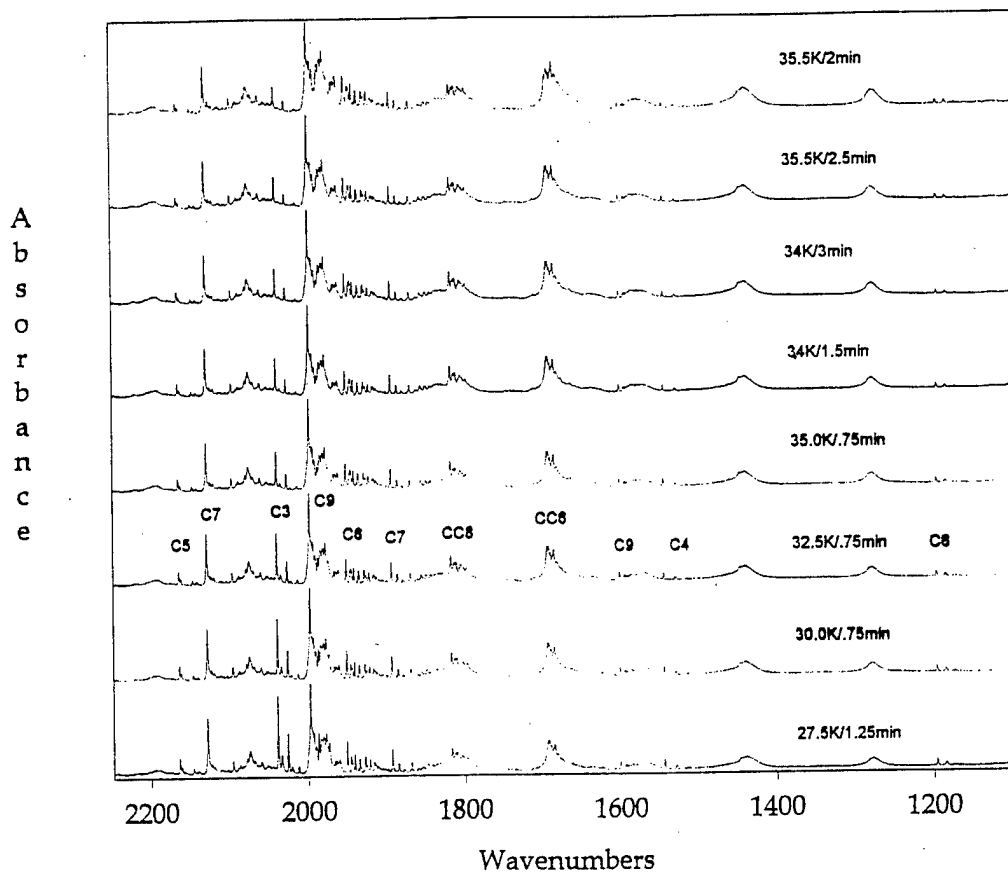


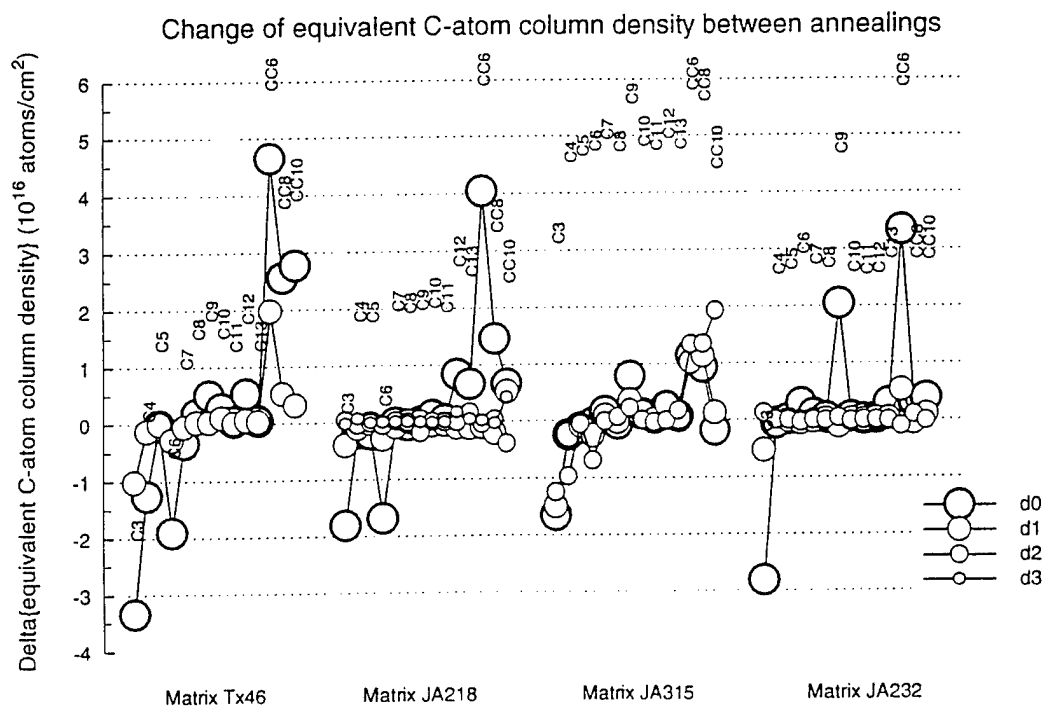
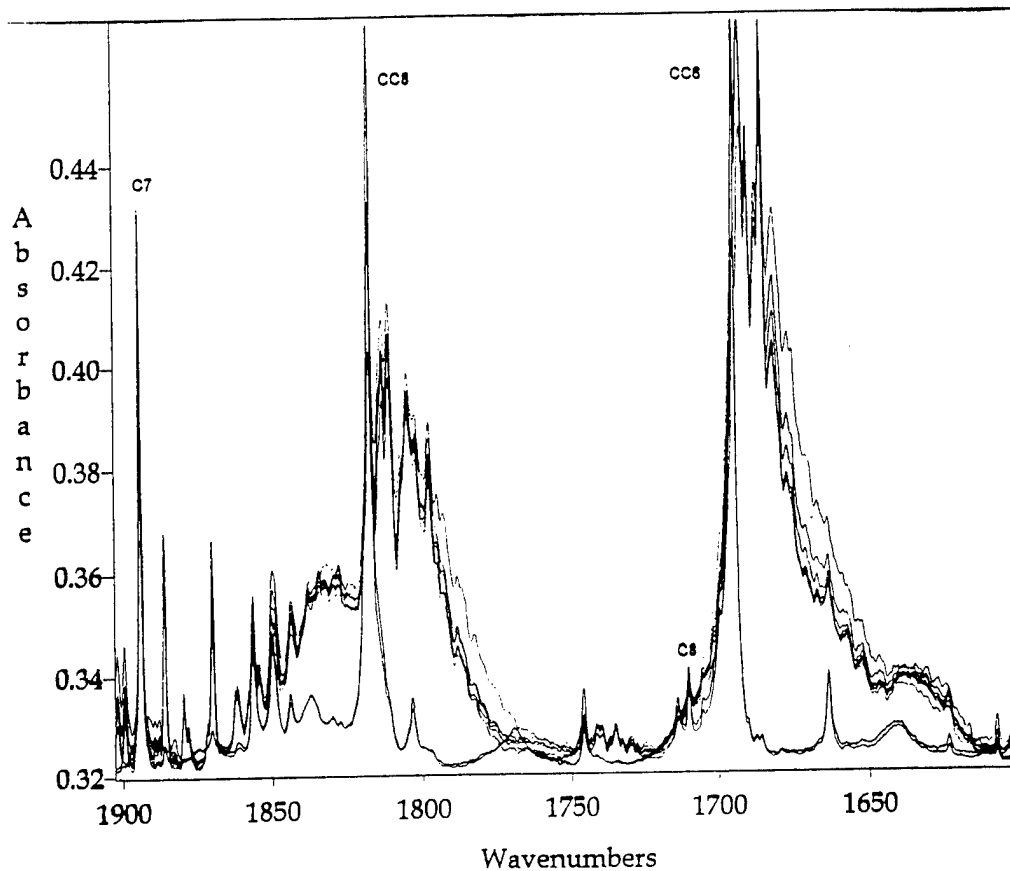


syn CC6 + LC8

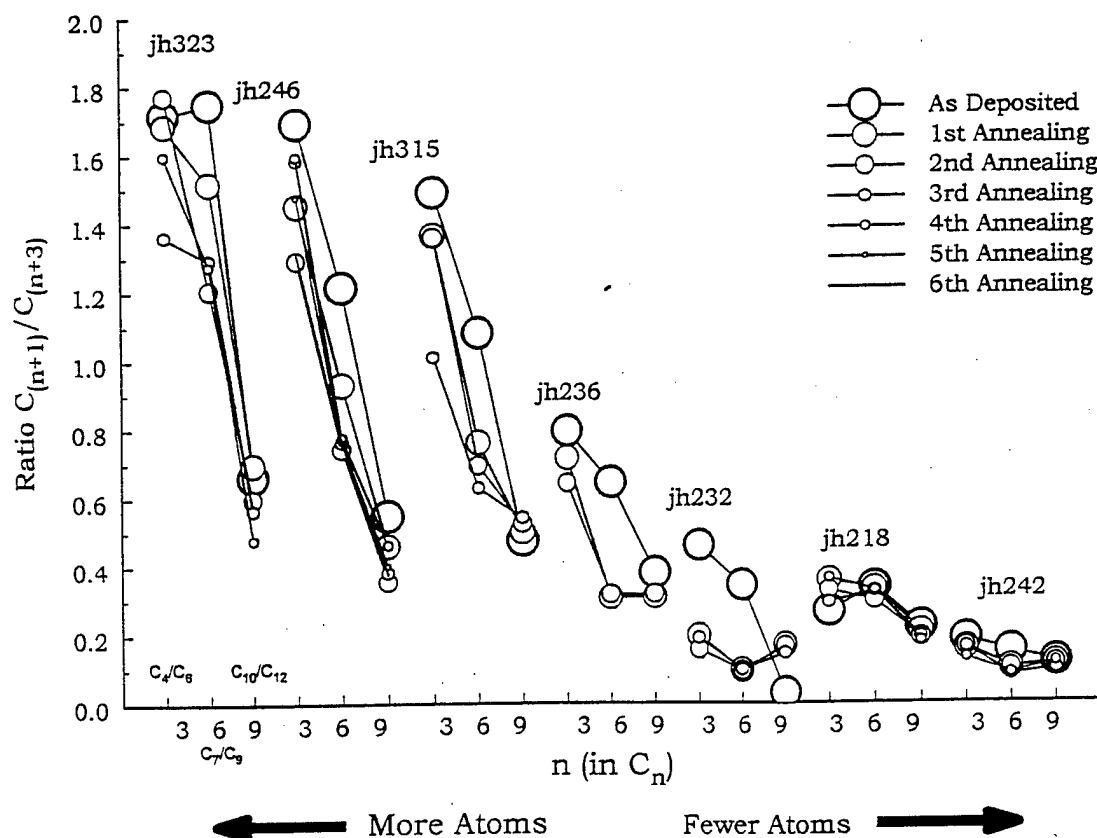


syn CC6 + LC8





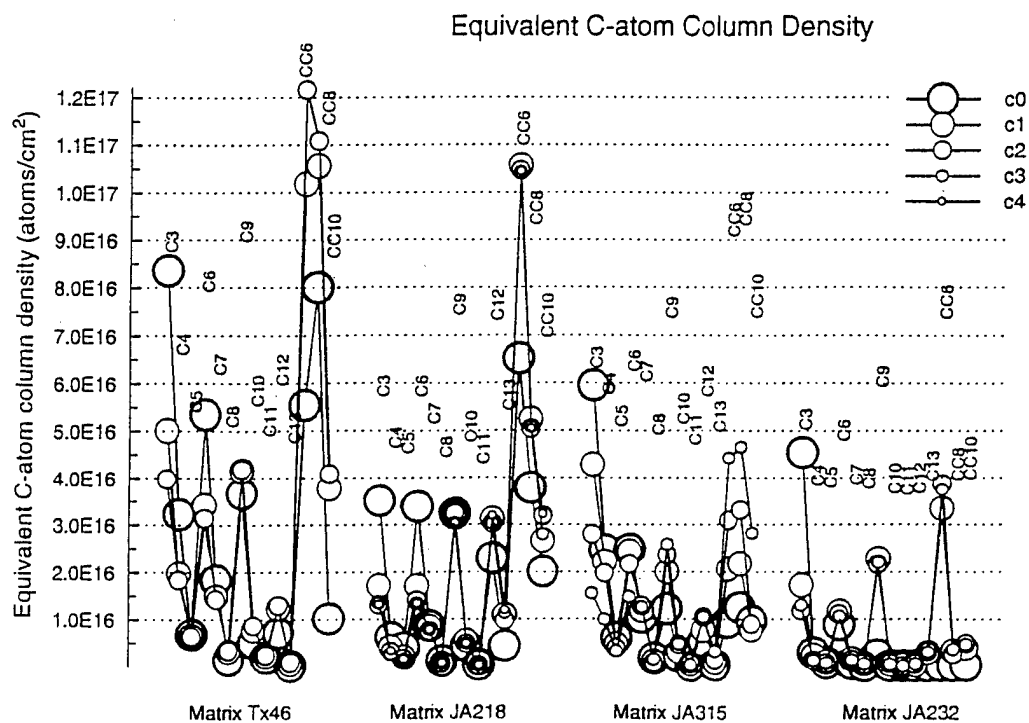
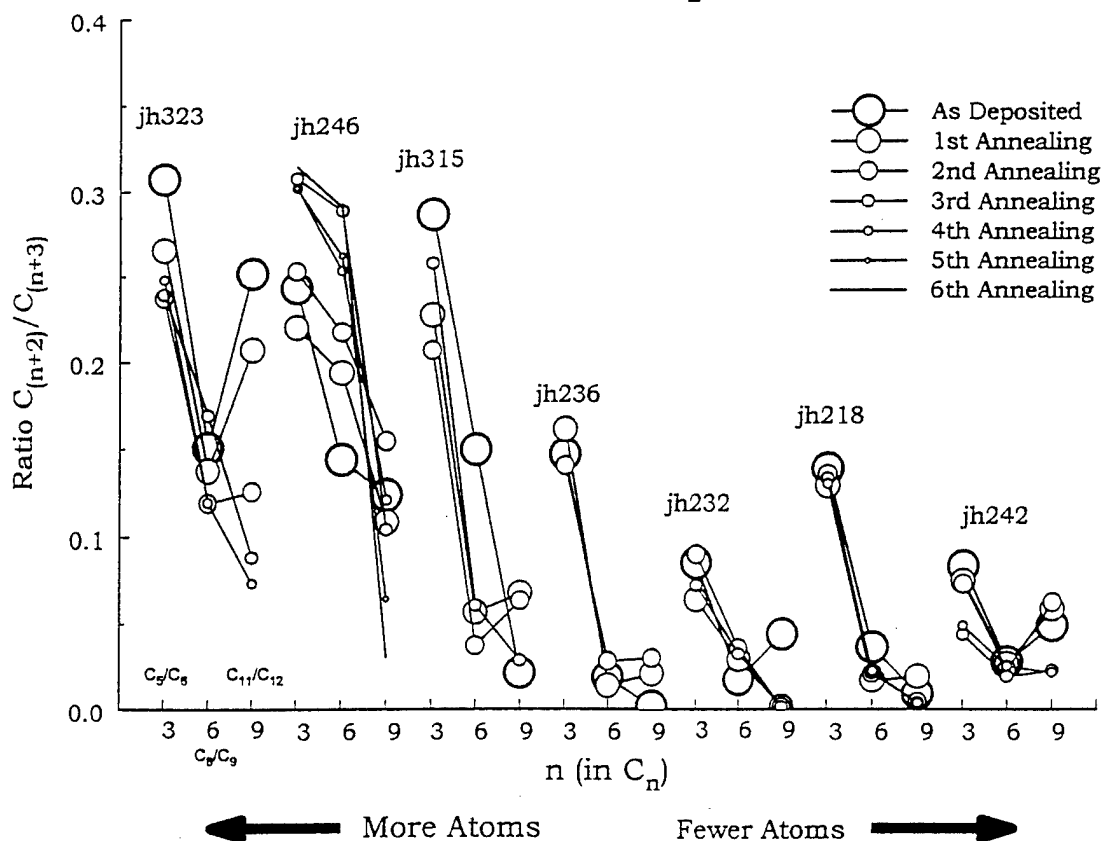
Comparison of C_4/C_6 , C_7/C_9 , C_{10}/C_{12} Ratios Obtained for Different Experimental Conditions



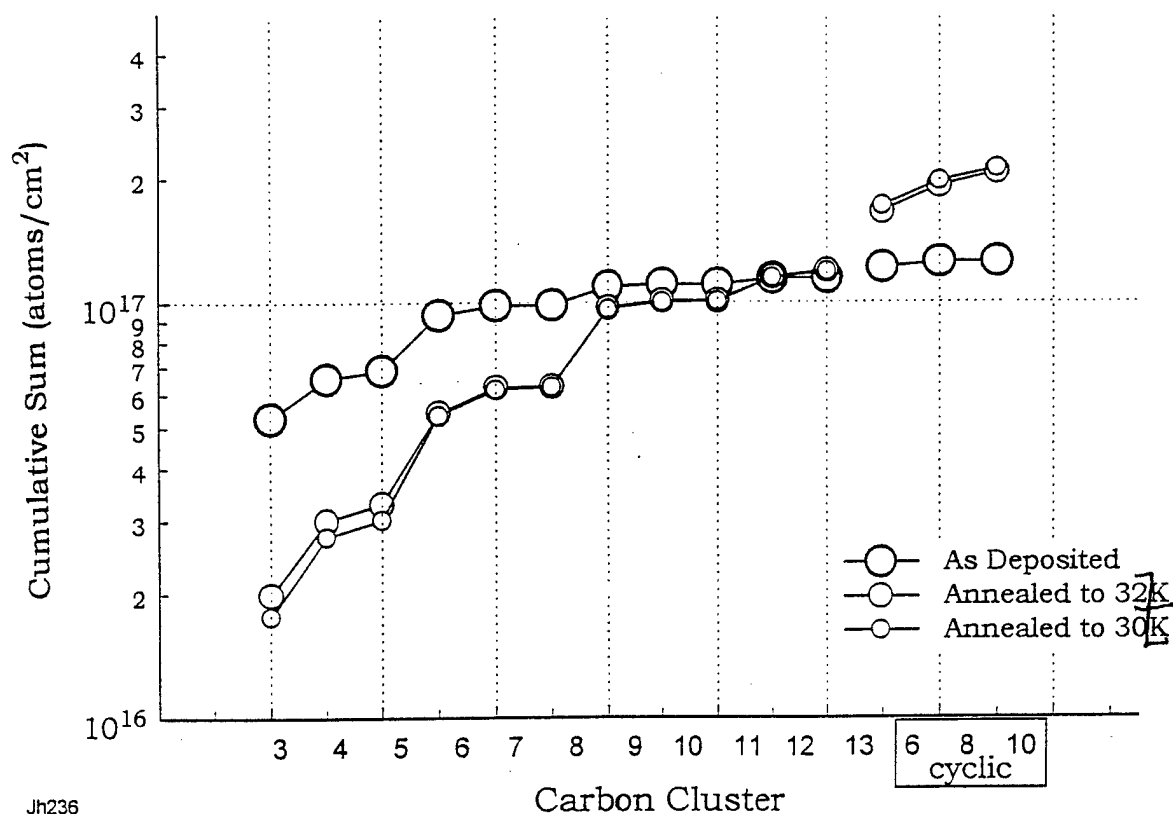
The ratio of the equivalent carbon atom column density for $n+1$ species (n as in C_n) to the equivalent carbon atom column density for $n+3$ species indicates how many atoms were available for formation of species like C_4 , C_7 , and C_{10} . When the Ta cell was hotter more $n+1$ species were formed during deposition than when the cell was colder. During annealings there were only minimal changes in the relative order of the ratios for C_4/C_6 ; C_7/C_9 ; C_{10}/C_{12} . Similar results are noted for $C(n+2)/C(n+3)$.

The run with 5% H_2 /95% Ar yields a lower $C(n+1)/C(n+3)$ ratio than would be expected. The hydrogen may be scavenging atoms.

Comparison of C_5/C_6 , C_8/C_9 , C_{11}/C_{12} Ratios Obtained for Different Experimental Conditions



Cumulative Sum of Equivalent Carbon Atom Density



Jh236

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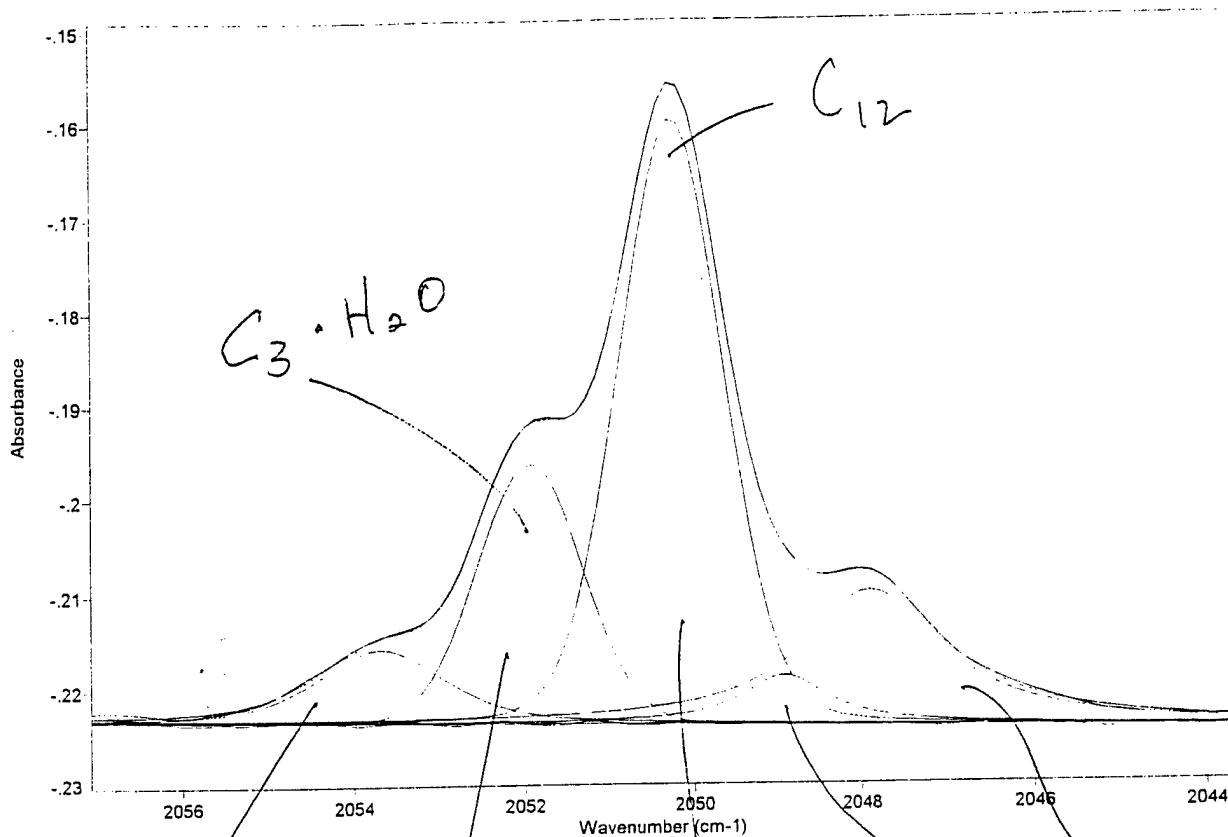
From successive cluster distributions one can calculate the quantity of carbon species that were not detected in the as-deposited matrix IR spectrum. This increase in the total equivalent carbon atom density is attributed to carbon atoms that are "invisible" to IR and were thus not accounted for in the original IR spectrum.

1= MixG+L (2053.7, .0078452, 1.7666, .44691)
 4= MixG+L (2048.9, .0052507, 1.2237, .99803)

2= MixG+L (2051.9, .027381, 1.4388, 1.00E-06)
 5= MixG+L (2047.9, .014253, 1.9605, .99103)

3= MixG+L (2050.3, .064283, 1.434, .10607)
 6= Quadr (-.41118, .000086926, 2.15E-09)

Jin



Cgrap501.spc
 Curve Fit
 Peaks
 Residual

$\lambda = 2053.7$
 Peak # $\rightarrow 1$
 width $\rightarrow 1.7$
 % Lorentzian $\rightarrow 44\%$

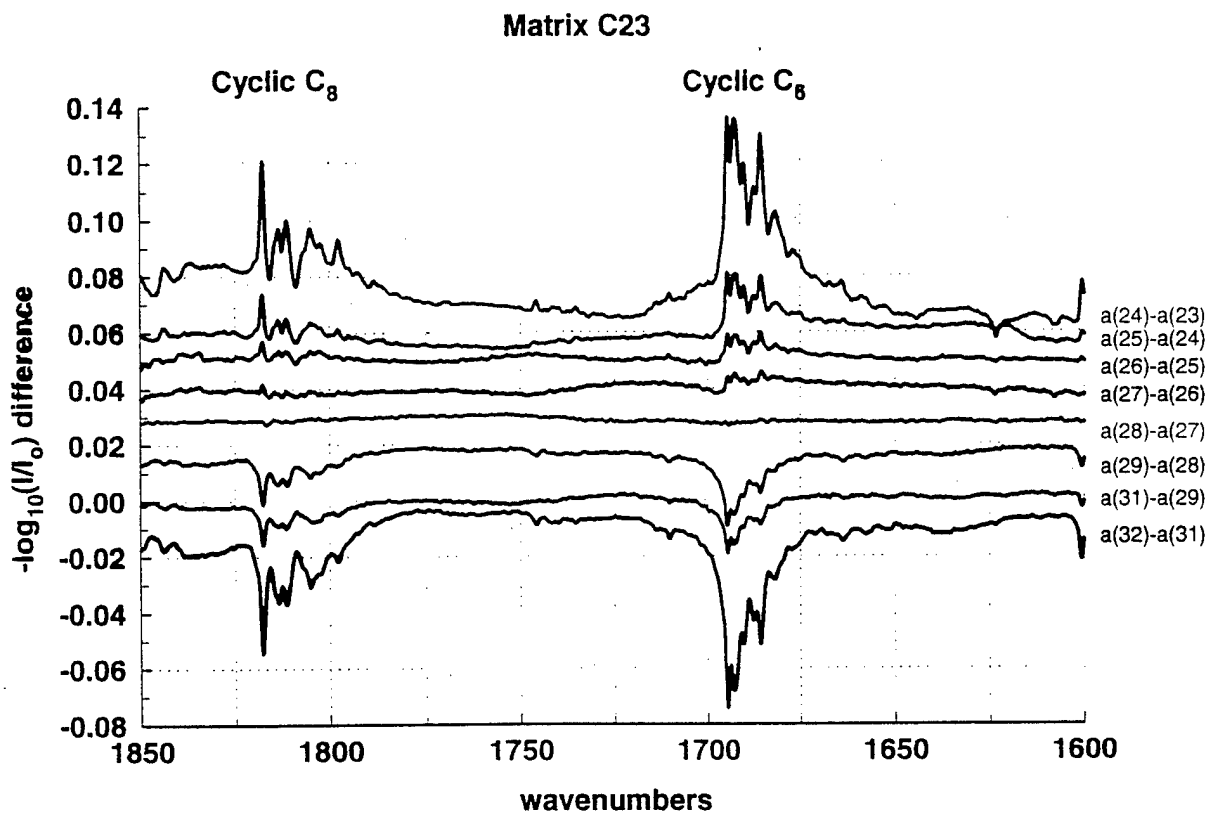
2051.9
 2
 1.4
 0%

2050.3
 3
 1.4
 10%

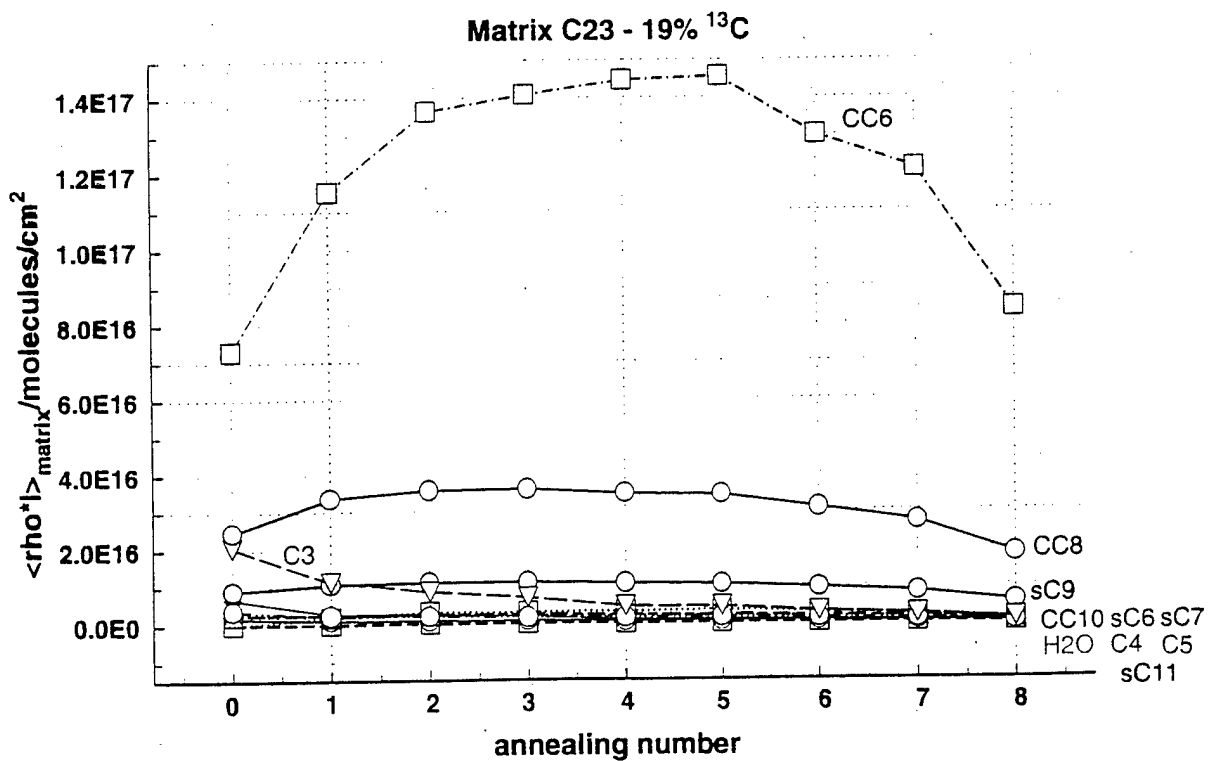
2047.9
 5
 1.9
 99%
 2048.9
 4
 1.2
 99%

Hanna Resler -
 calcd w/ Wtting (3f)

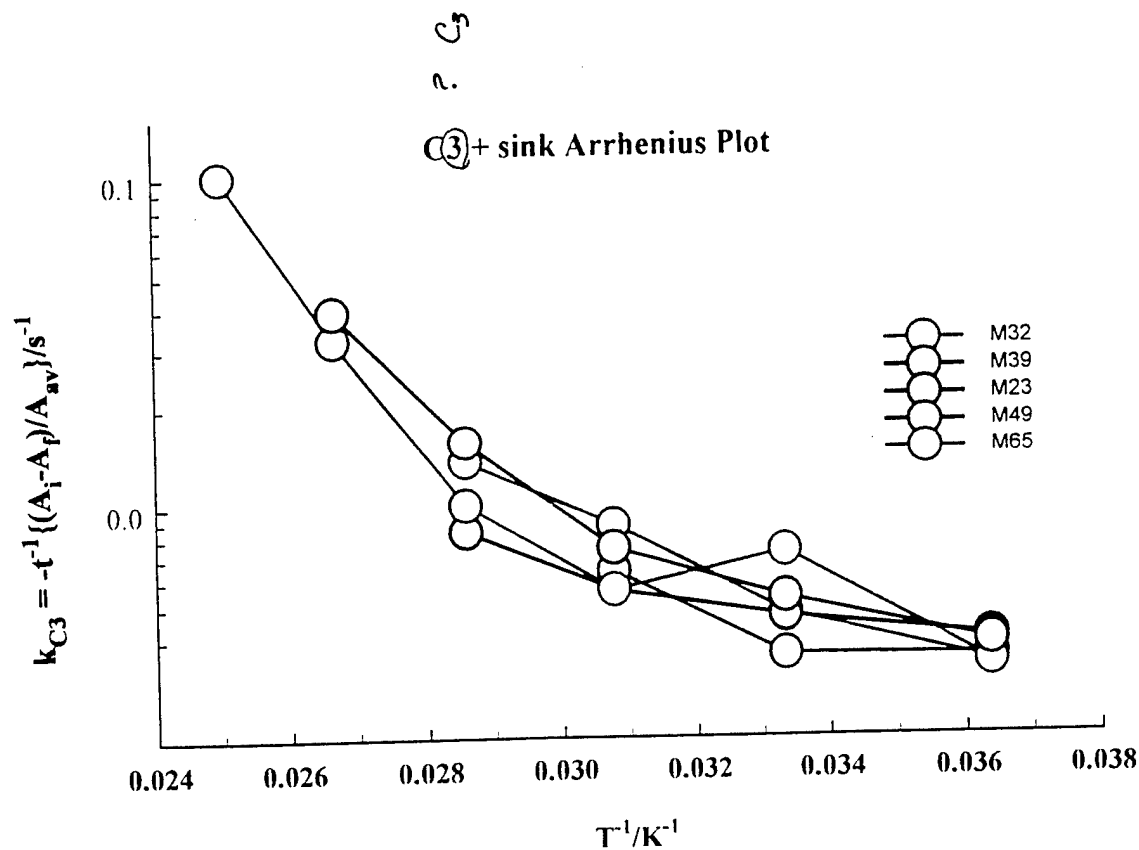
1L



c6dif233.axg Phillips Lab, Edwards AFB, CA 93524 Sept. 11, 1997 3:15:09 PM

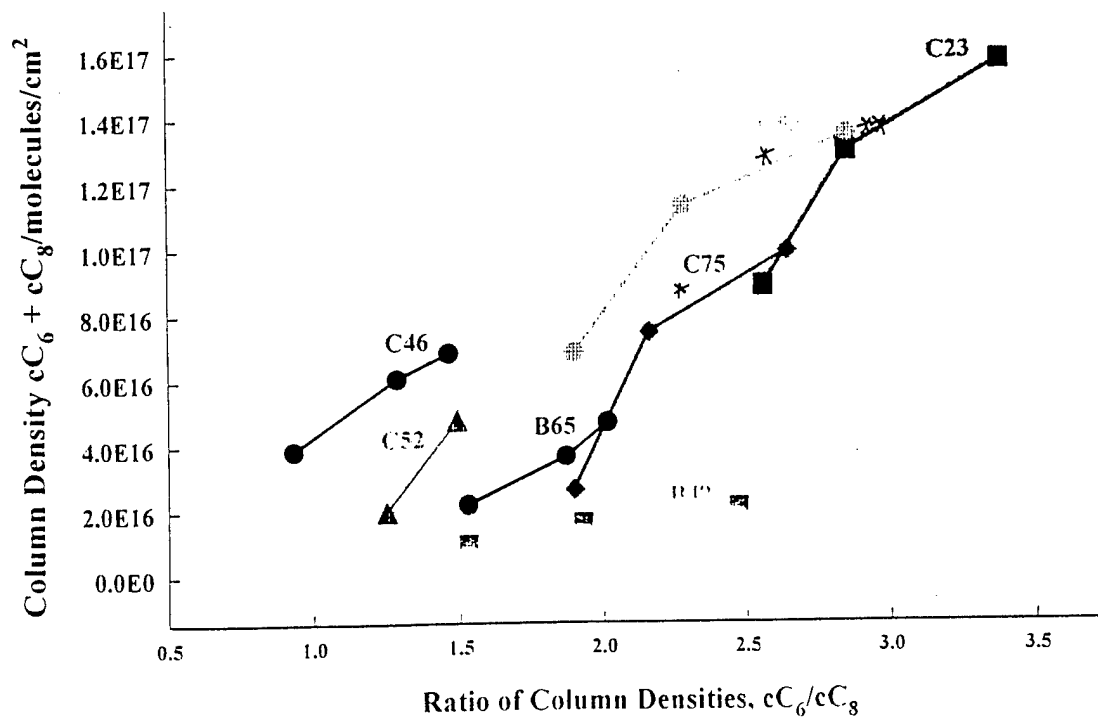


C23c2a.axg

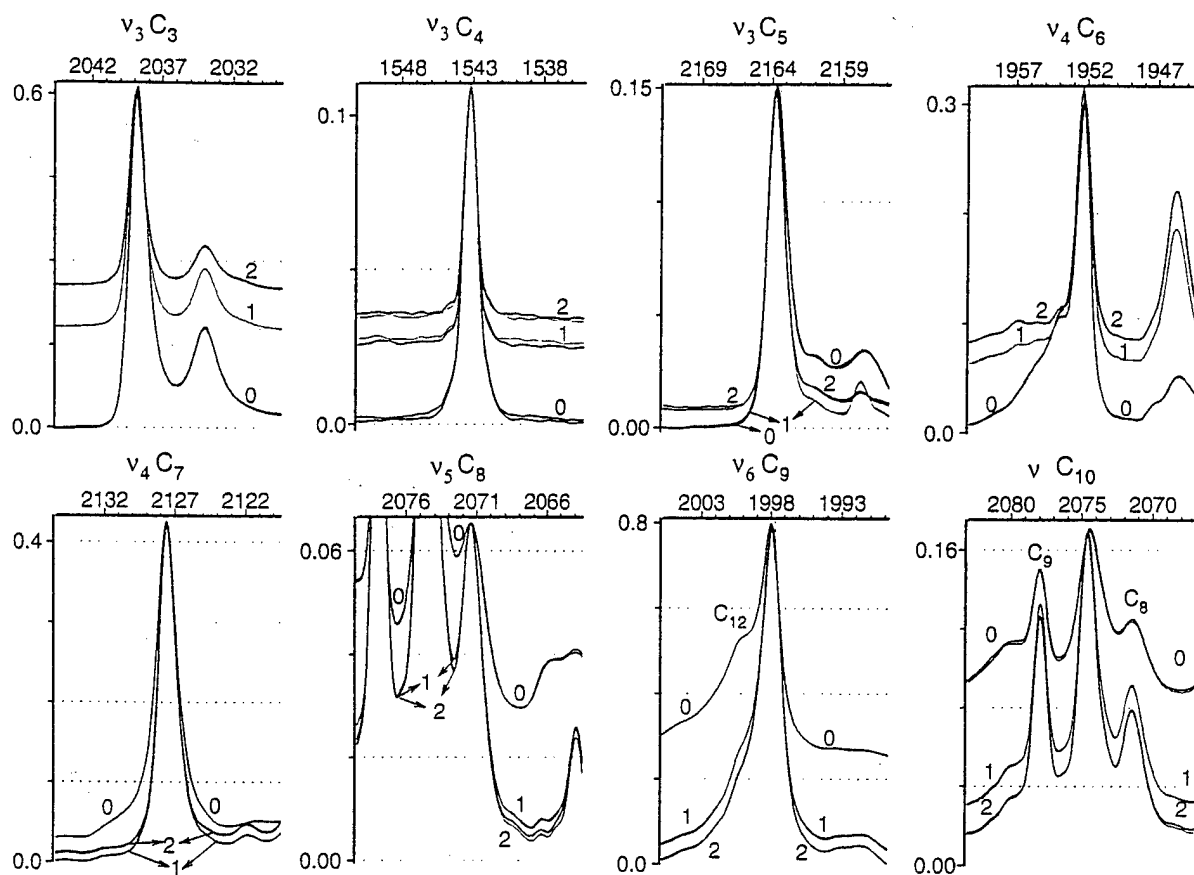


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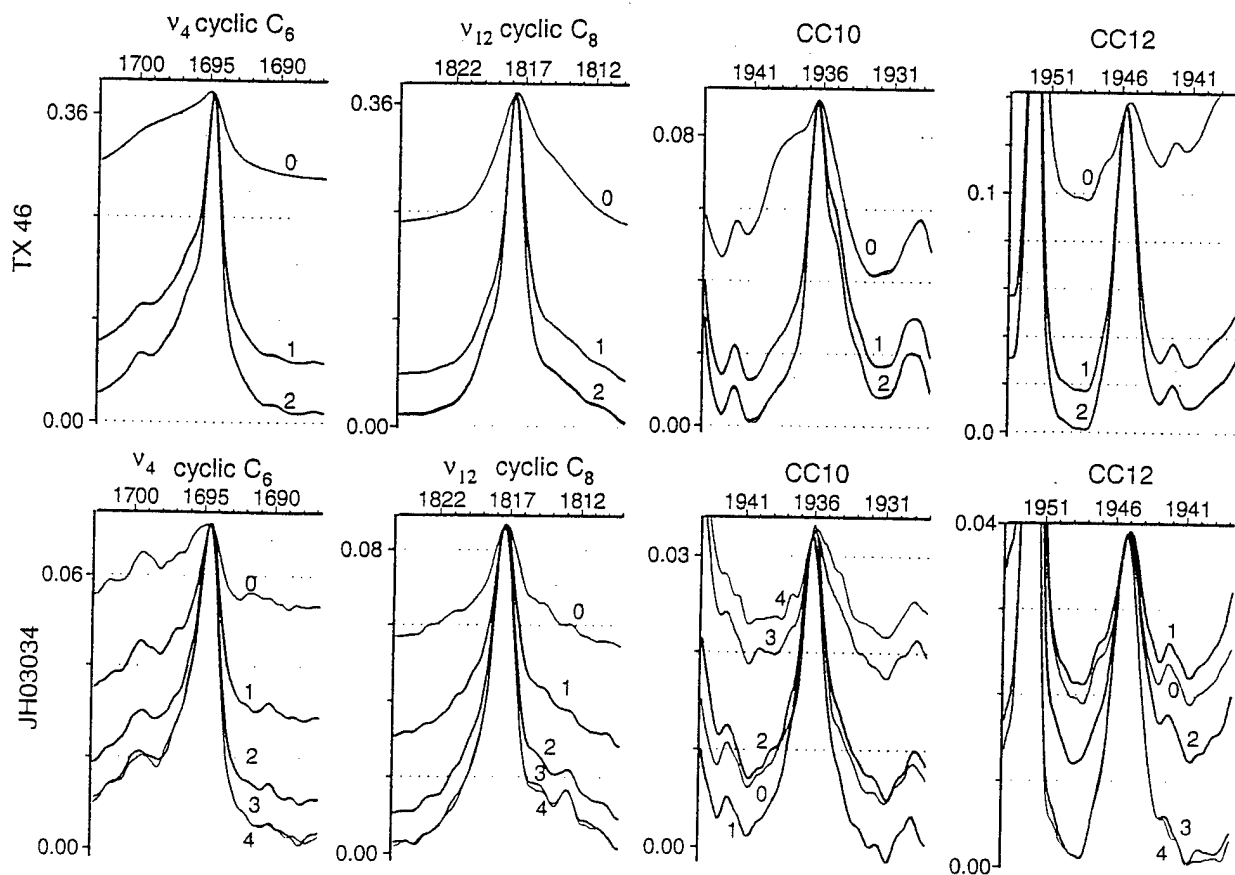
Cyclic C₆ and Cyclic C₈ in High Carbon Density Hedm Prototypes,



MhiDsmv1.axg



Carbon Matrix (a) - C_n Clusters



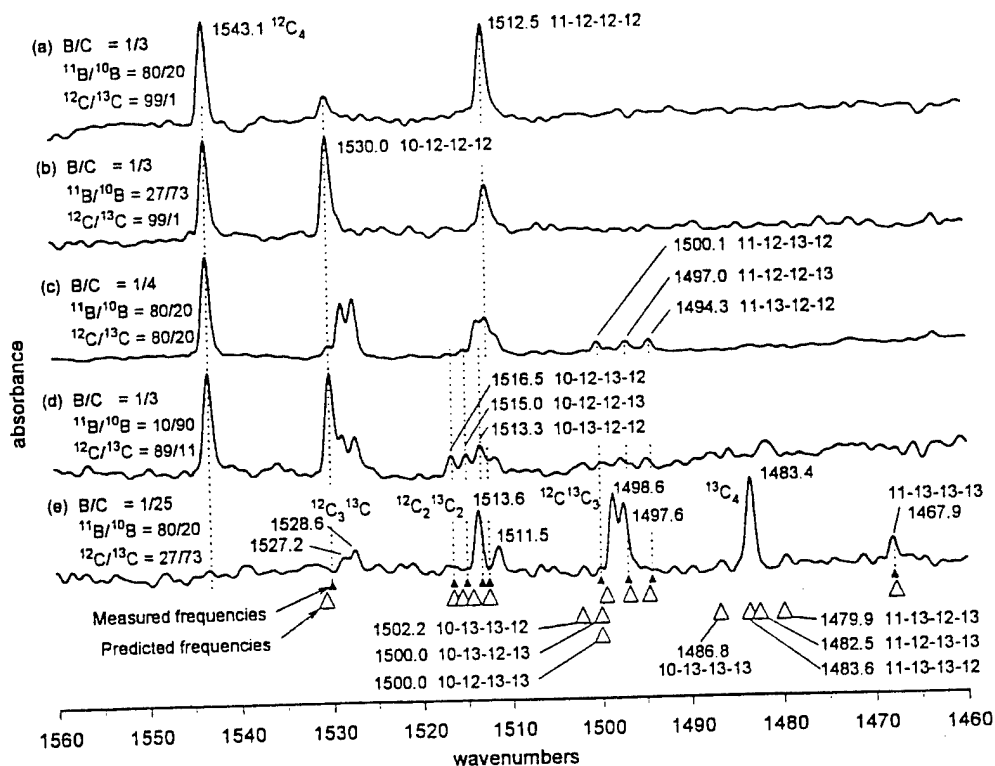


FIG. 1. FTIR spectra of the $\nu_2(\sigma)$ mode of isotomers of linear BC_3 and the $\nu_3(\sigma_a)$ mode of isotomers of linear C_4 . The spectra were recorded at 10 K after annealing the matrices with the indicated compositions at 27.5 K for 150 s. The large open triangles at the bottom show the predicted frequencies of linear BC_3 isotomers (as explained in the text) and small filled triangles show measured isotomer frequencies.

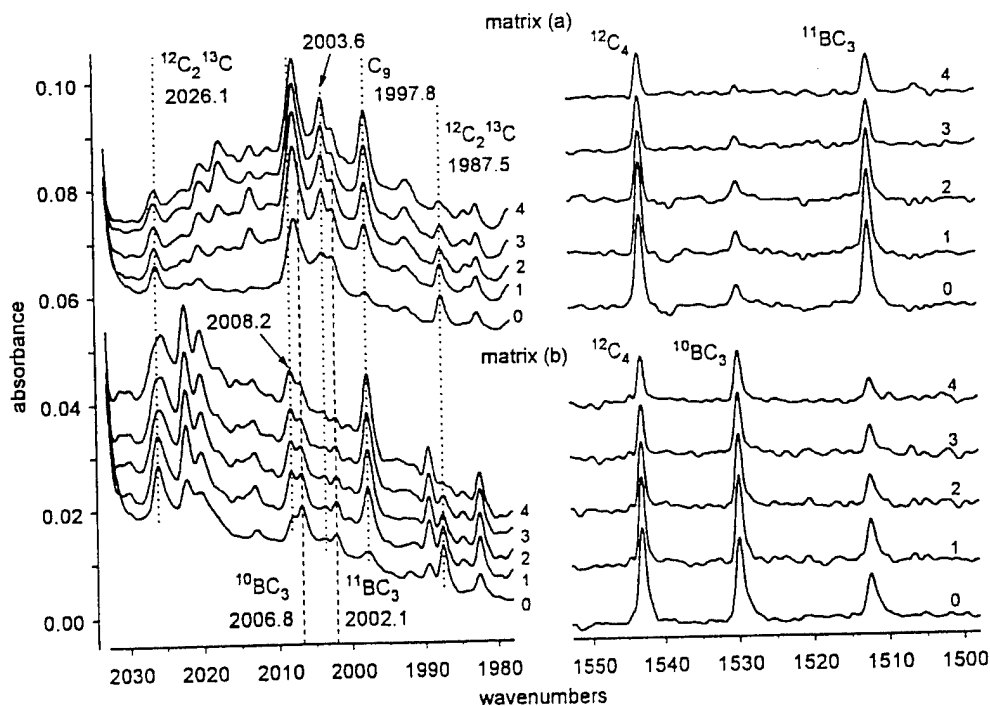


FIG. 2. Spectra obtained from matrix (a) [$^{11}B/^{10}B = 4/1$] and matrix (b) [$^{11}B/^{10}B = 1/2.7$] showing correlation upon annealing of the $\nu_1(\sigma)$ bands of $^{10}BC_3$ and $^{11}BC_3$ at 2066.8 and 2002.1 cm^{-1} with the $\nu_2(\sigma)$ bands at 1530.0 and 1512.5 cm^{-1} . The spectra labeled "0" are from the originally deposited matrix. Labels "1" to "4" indicate spectra recorded after the first through fourth annealing as follows: (1) 27.5 K for 150 s, (2) 30.0 K for 75 s, (3) 32.5 K for 45 s, (4) 35.0 K for 30 s. Frequency and absorbance scales are identical for all spectra. The plotted absorbance is $-\log_{10}$ of the transmittance. To facilitate comparisons between matrices, the absorbance of the matrix (b) spectra are multiplied by 1.4.

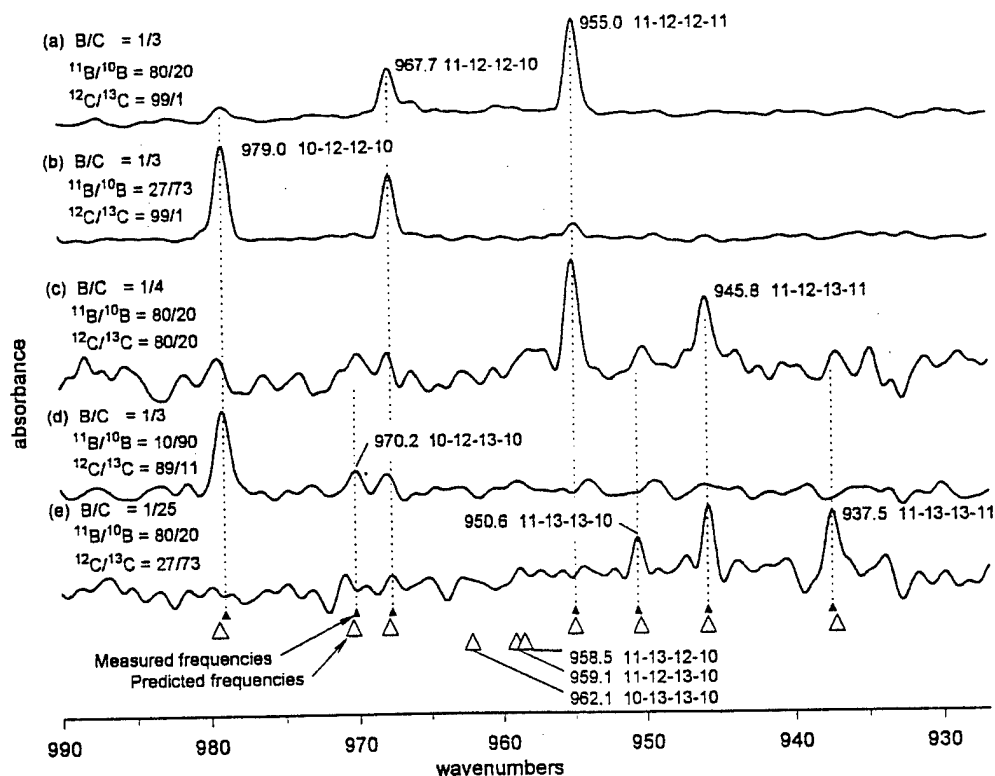


FIG. 3. FTIR spectra of the $\nu_3(\sigma_u)$ mode of isotopomers of linear BCCB. The spectra were recorded after annealing the matrices with the indicated compositions at 27.5 K for 150 s. The large open triangles at the bottom show the predicted frequencies of linear BCCB isotopomers (as explained in the text) and small filled triangles show measured isotopomer frequencies.

TABLE IV. Experimental B_2C_2 isotopomer frequency patterns. Frequencies and frequency intervals (cm^{-1}) in triplet bands of B_2C_2 isotopomers.

Boron isotope triplets				Carbon isotope triplets			
Isotopomer	Freq.	Intervals		Isotopomer	Freq.	Intervals	
		Short	Long			Short	Long
$^{10}B_2\ ^{12}C_2$	979.0	11.3		$^{10}B_2\ ^{12}C_2$	979.0	8.8	
$^{10,11}B_2\ ^{12}C_2$	967.7	12.7	24.0	$^{10}B_2\ ^{12,13}C_2$	970.2	(7.9) ^a	(16.7) ^a
$^{11}B_2\ ^{12}C_2$	955.0			$^{10}B_2\ ^{13}C_2$	(962.3) ^a		
$^{10}B_2\ ^{12,13}C_2$	970.2	(11.5) ^a		$^{10,11}B_2\ ^{12}C_2$	967.7	(9.0) ^a	
$^{10,11}B_2\ ^{12,13}C_2$	(958.7) ^a	(12.9) ^a	24.4	$^{10,11}B_2\ ^{12,13}C_2$	(958.7) ^a	(8.1) ^a	17.1
$^{11}B_2\ ^{12,13}C_2$	945.8			$^{10,11}B_2\ ^{13}C_2$	950.6		
$^{10}B_2\ ^{13}C_2$	(962.3) ^a	(11.7) ^a		$^{11}B_2\ ^{12}C_2$	955.0	9.2	
$^{10,11}B_2\ ^{13}C_2$	950.6	13.1	(24.8) ^a	$^{11}B_2\ ^{12,13}C_2$	945.8	8.3	17.5
$^{11}B_2\ ^{13}C_2$	937.5			$^{11}B_2\ ^{13}C_2$	937.5		

^aFrequencies and intervals in parentheses were interpolated or extrapolated from measured quantities.

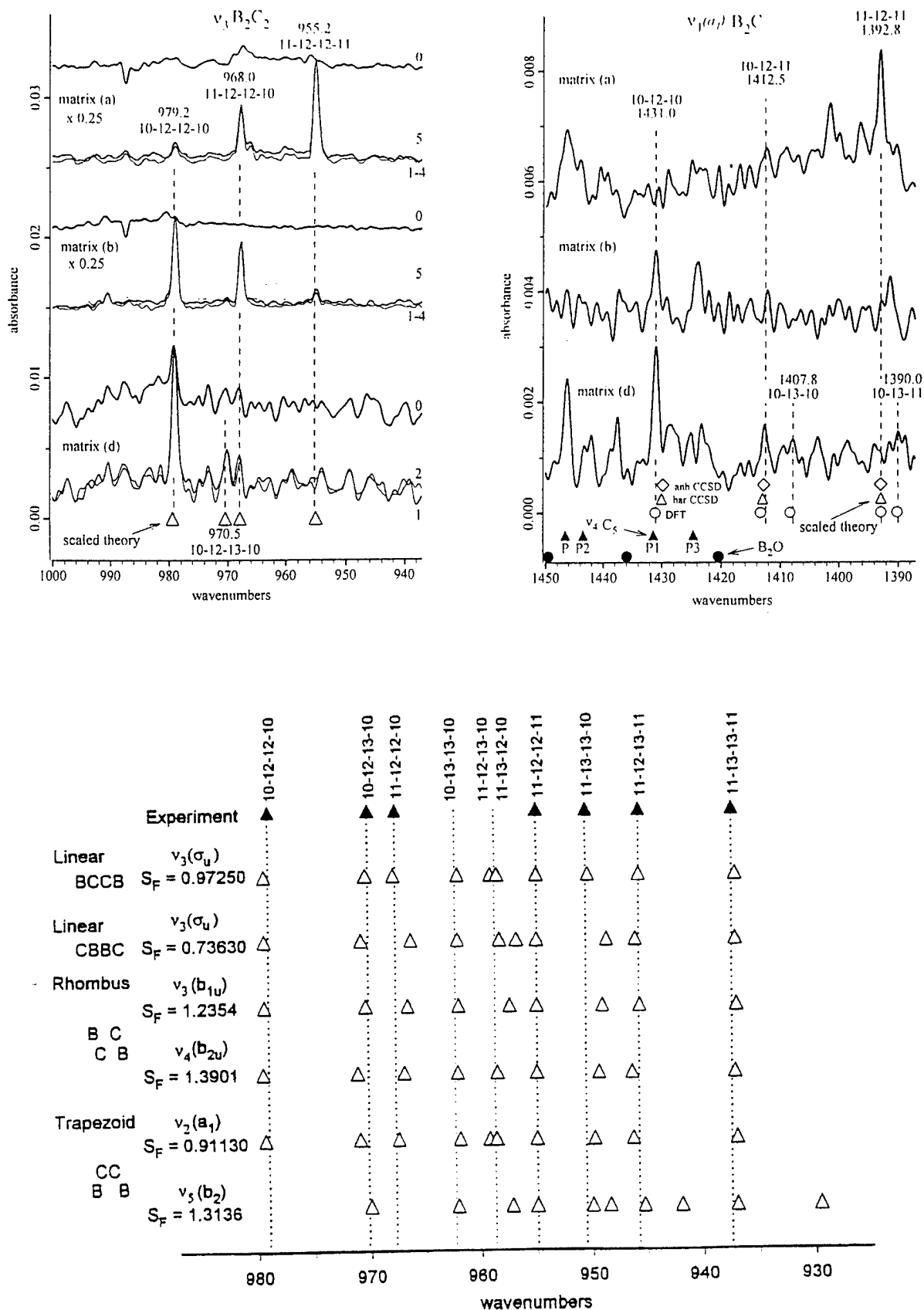
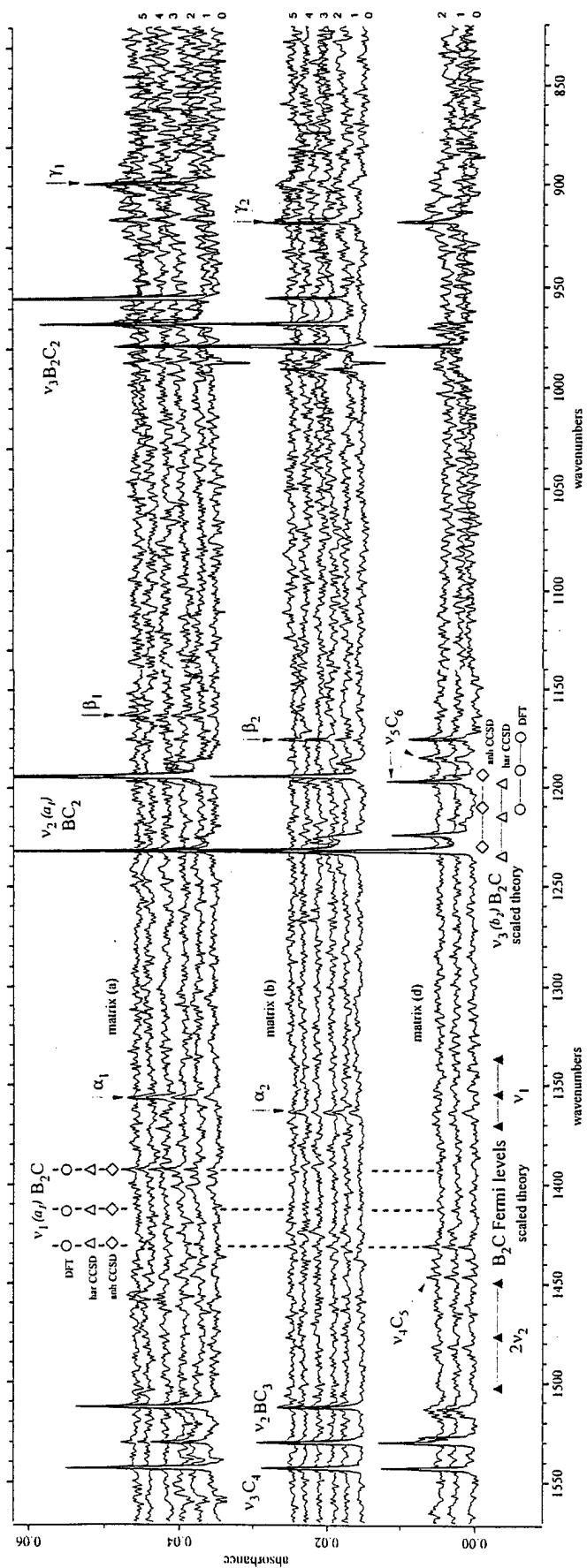
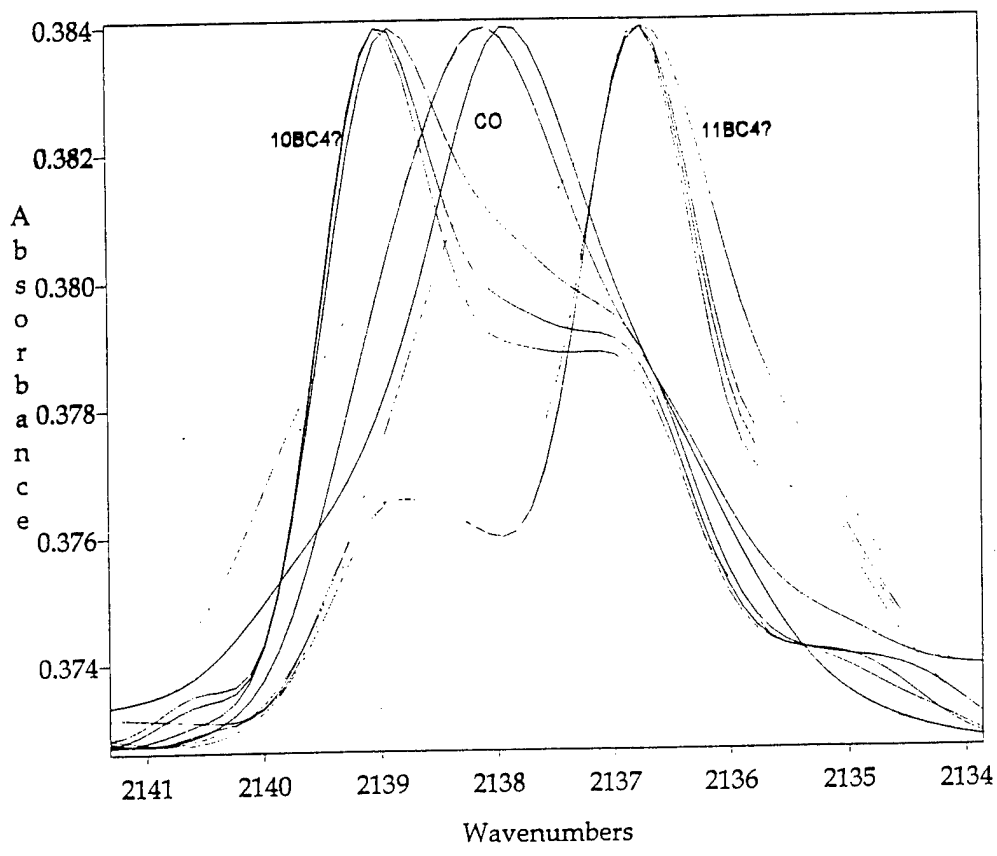
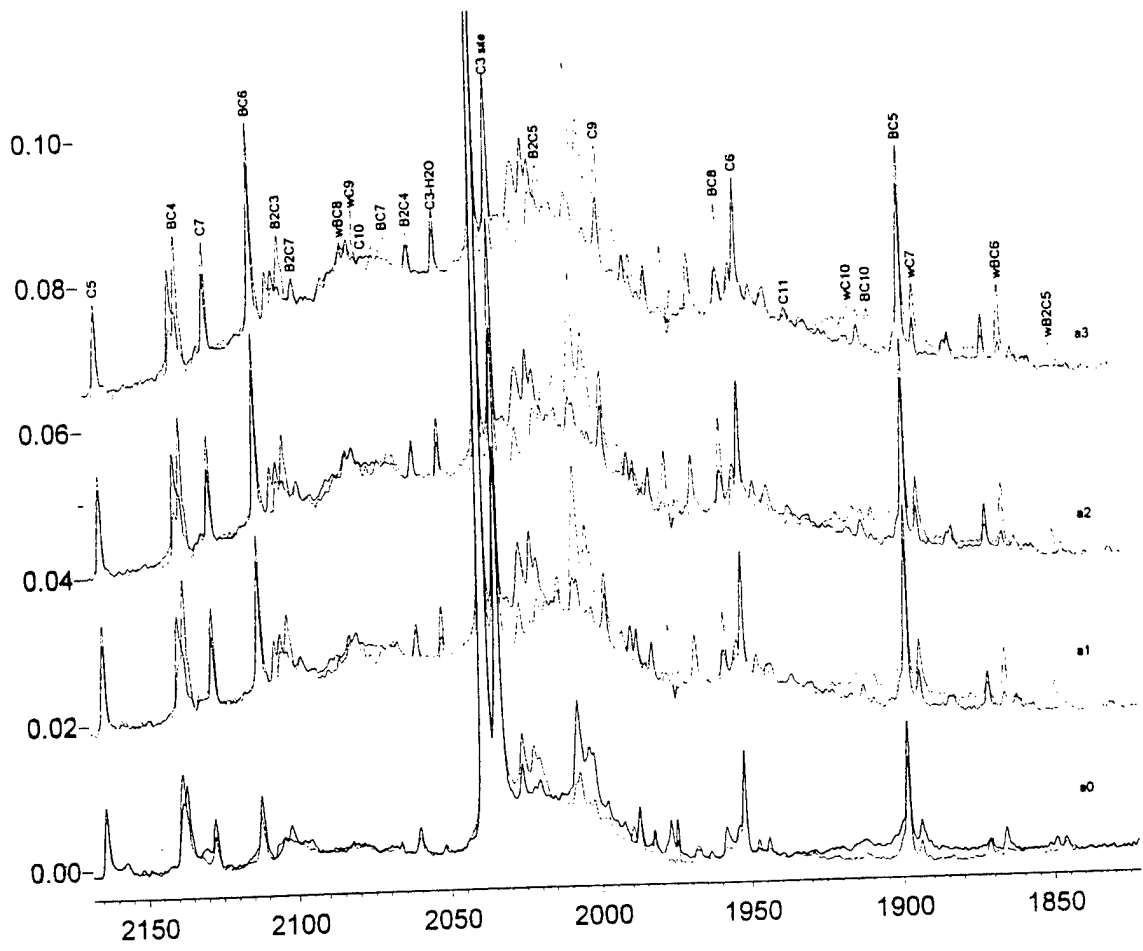
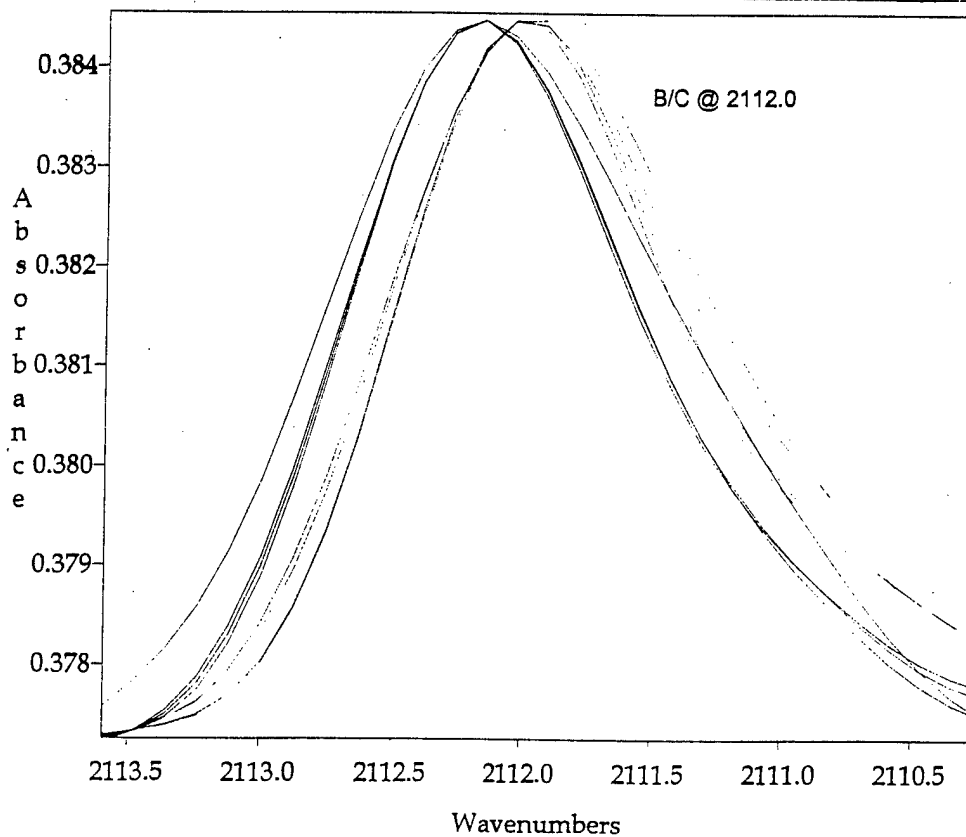
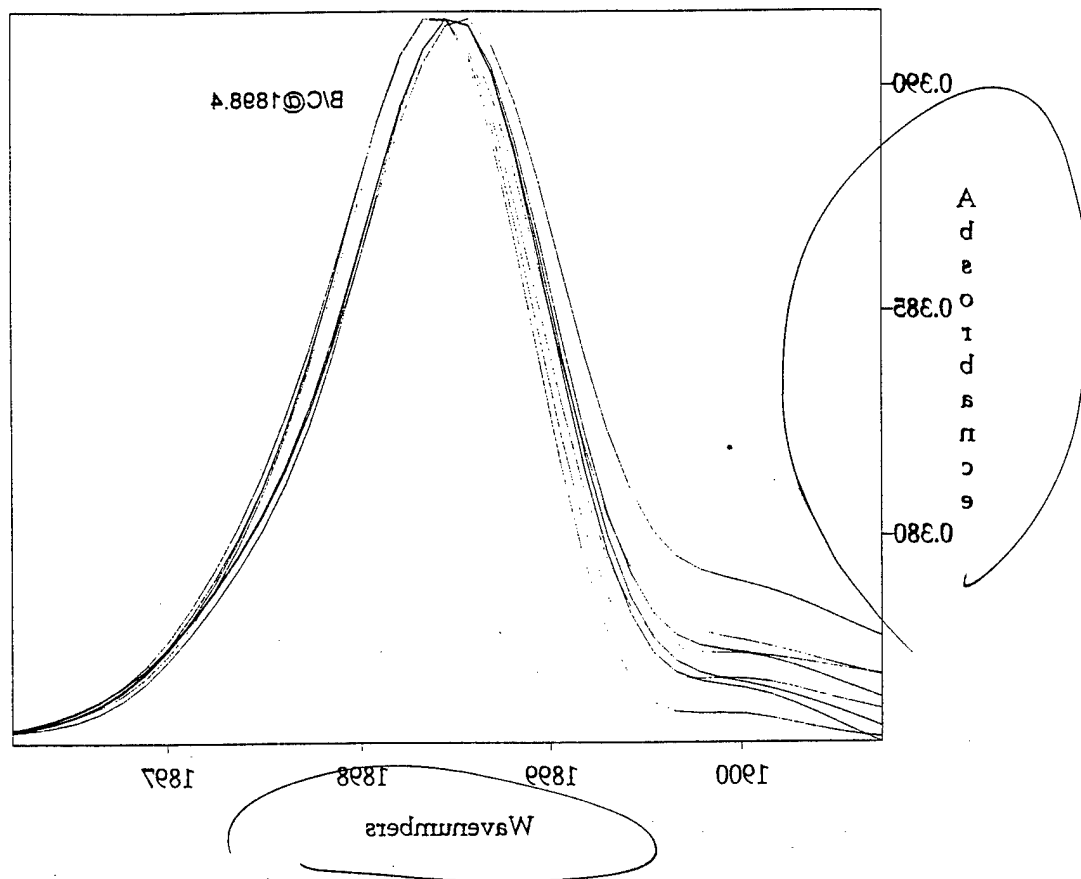
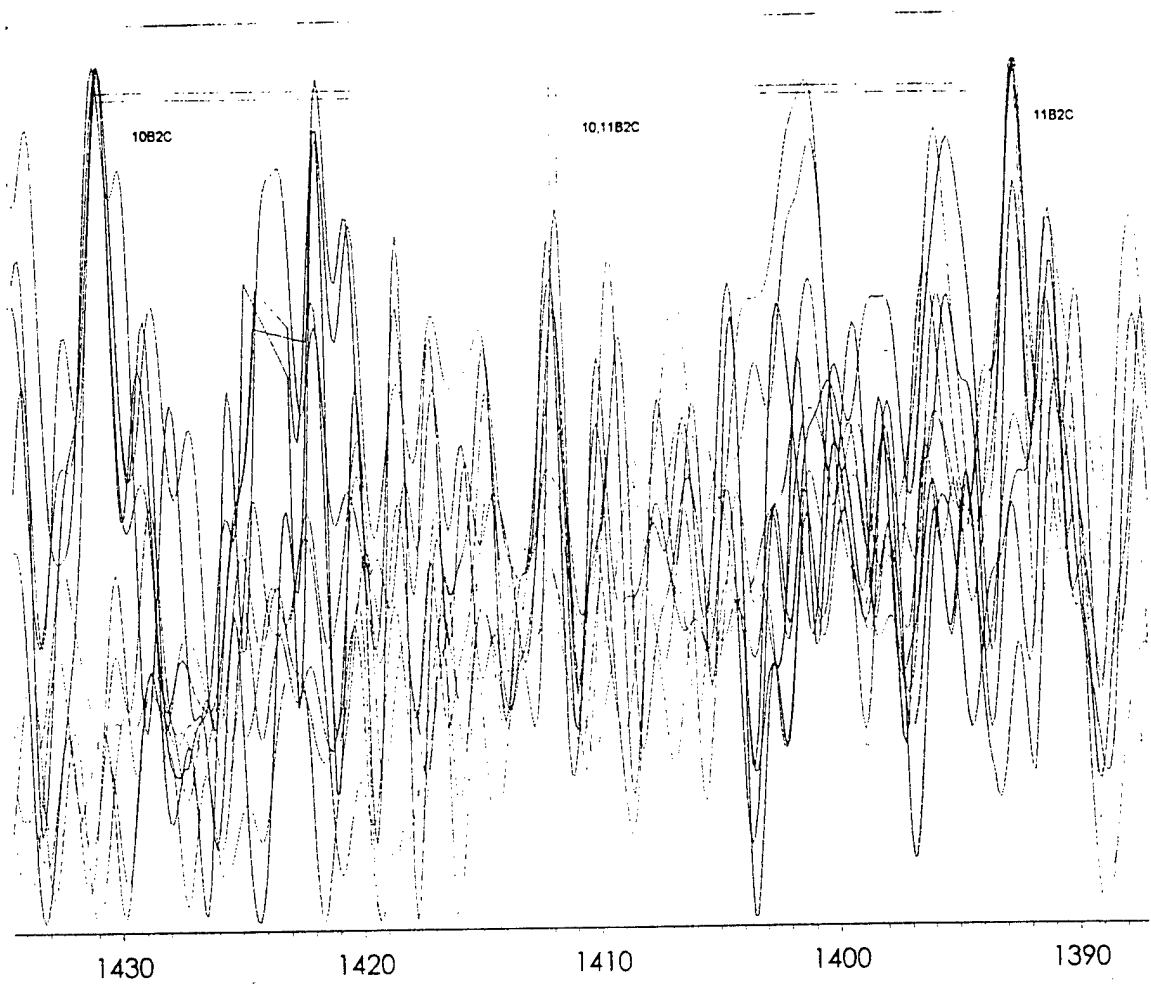


FIG. 4. Comparison of experimental isotopomer frequencies to scaled theoretical isotopomer frequencies for the most intense modes of four B_2C_2 geometries as calculated by Rittby, Ref. 5.









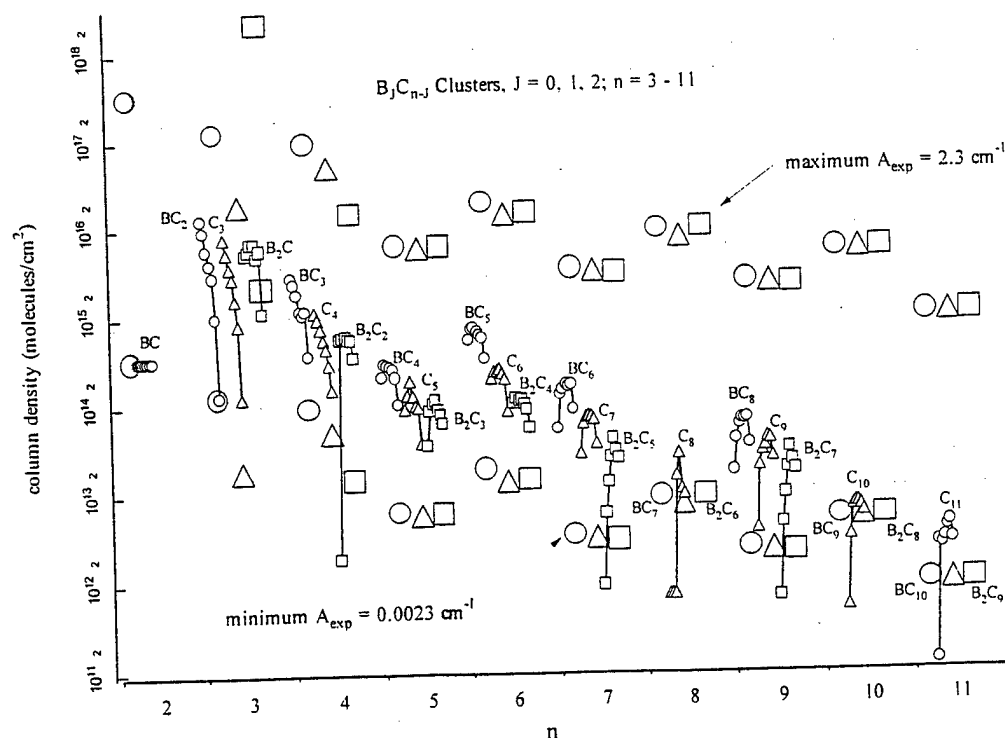
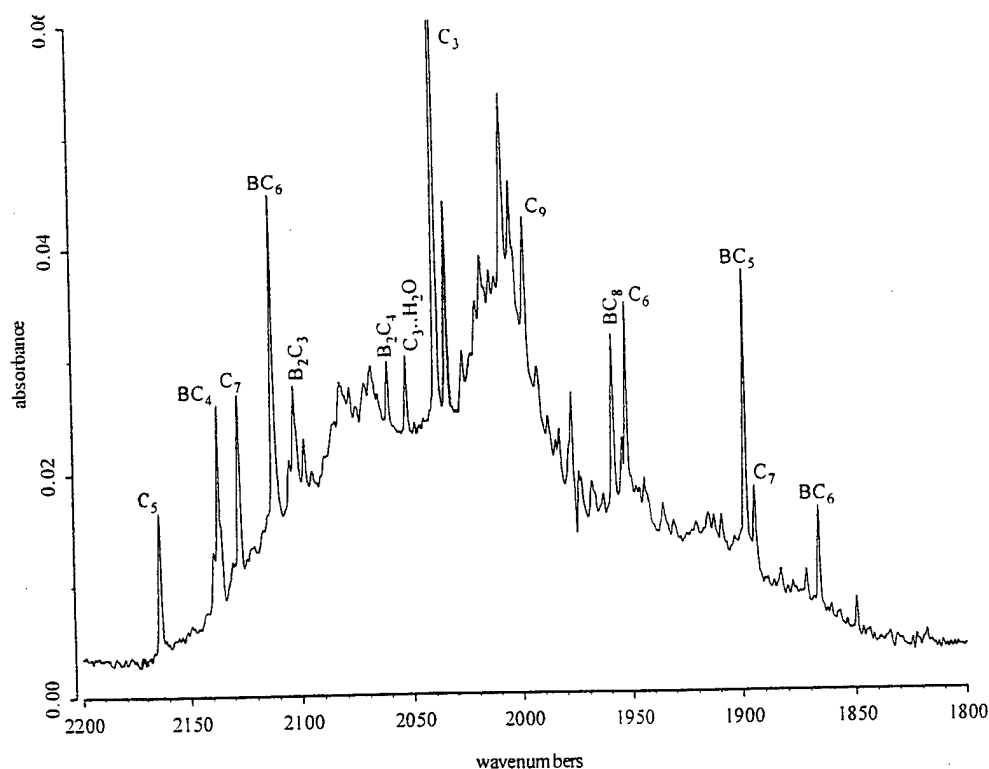


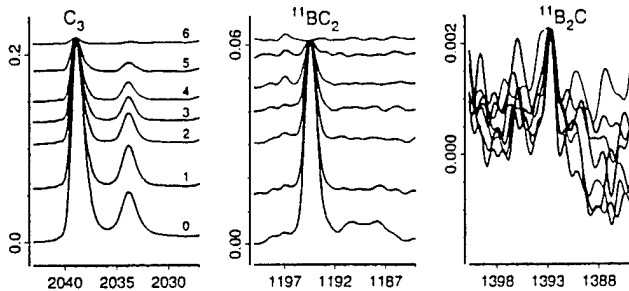
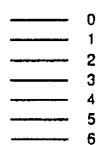
Figure 1. Distribution of B_nC_{n-1} clusters. $J = 0, 1, 2; n = 3 - 11$. Circles, triangles and squares represent BC_{n-1} , C_n , and BC_{n-2} clusters, respectively. Large symbols denote upper and lower limits of measurement, based on a nominal minimum measurable absorbance of 0.0023 cm^{-1} , and a maximum absorbance for linearity of Beer's law of 2.3 cm^{-1} (1% transmittance). Small symbols denote measured quantities in the initial matrix, and in six annealed matrices. Annealing temperatures and times were (1) 27.5 K/150 s, (2) 30.0 K/75 s, (3) 32.5 K/45 s, (4) 35.0 K/30 s, (5) 37.5 K/20 s, (6) 40.0 K/20 s. The decreases in column density in the fifth and sixth annealing are due to matrix sublimation. Some of the larger clusters ($n = 8, 10, 11$) have not been identified, BC_7 , B_2C_6 , BC_9 , B_2C_8 , BC_{10} , B_2C_9 .

$J = 0 \quad 1 \quad 2$

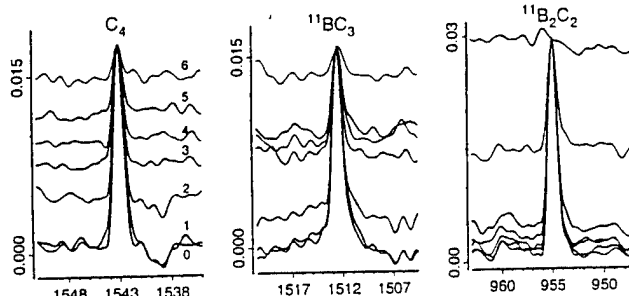
matrix (a): $^{11}\text{B}/^{10}\text{B} = 80/20$, $^{12}\text{C}/^{13}\text{C} = 99/1$

$n = 3$

annealing

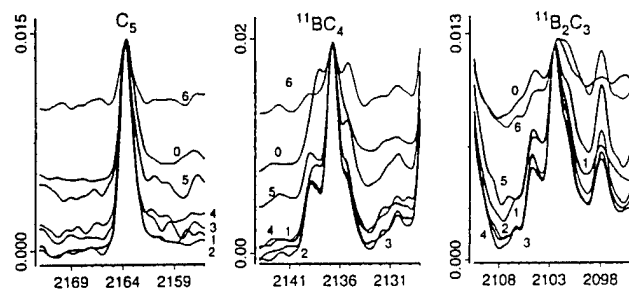
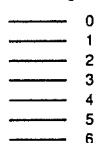


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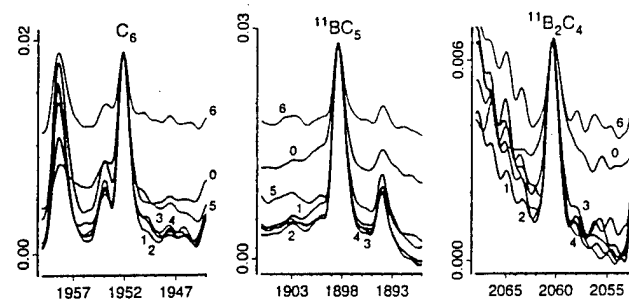


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annealing

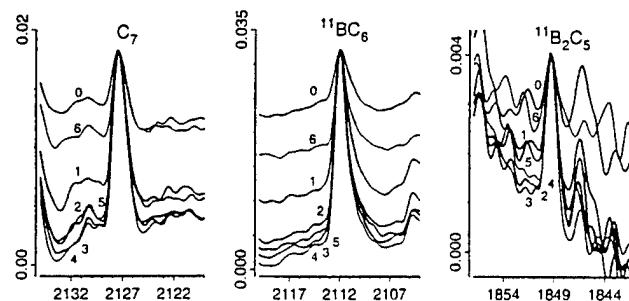
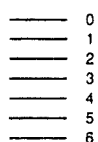


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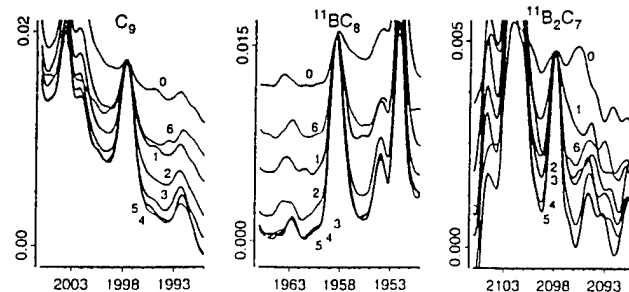


7

annealing



9



Conclusions

Linear C_3 , cyclic BC_2 , and cyclic B_2C , constituted about 80% of the total observable boron and carbon in the initially deposited matrix, but B_3 was not observed.

The measured trimer distribution in the initially formed matrices was

$$\rho(C_3) : \rho(BC_2) : \rho(B_2C) : \rho(B_3) \sim 1 : 1.5 : 0.5 : < 0.05.$$

Statistical substitution of J boron atoms into an n -atom carbon cluster produces a distribution given by $\rho(B_J C_{n-J}) / \rho(C_n) = \{n(n-1)\dots(n-J+1)\} / J! [B/C]^J$. With the experimental $B/C \sim 1/3$, the statistical trimer distribution is

$$\rho(C_3) : \rho(BC_2) : \rho(B_2C) : \rho(B_3) \sim 1 : 1 : 0.33 : 0.03.$$

Agreement between distributions implies trimers form by random condensation of well-mixed atoms, uninfluenced by the relative energies of the trimers, the energies of their precursors, or preferential kinetics pathways that could otherwise distort the statistics.

Linear C_3 and cyclic BC_2 , disappeared entirely when the matrices were repeatedly annealed to temperatures between 25 K and 35 K, but cyclic B_2C was inert.

Linear C_4 and BC_3 (BCCC) disappeared more slowly, and linear B_2C_2 (BCCB) grew to $\sim 95\%$ of its final value during the first annealing. B_2C_2 was also inert, as B_2C .

The sources of B_2C_2 are from condensation of atom plus trimer ($B + BC_2$ but not $C + B_2C$) or dimer + dimer ($BC + BC$ but not $B_2 + C_2$). Although BC was not observed, the upper limit of $\rho(BC)$ is larger than $\rho(B_2C_2)$ so that BC cannot be ruled out as a source of B_2C_2 .

The growth of B_2C_2 is conclusive evidence of the presence of BC and/or B in the originally deposited matrix in an amount at least as great as the growth of B_2C_2 .

Linear C_5 , BC_4 (BCCCC) and B_2C_3 (BCCCB) and larger linear clusters ($B_J C_{n-J}$, $5 < n < 11$, $J = 0, 1, 2$), all grew upon annealing.

The sources of B_2C_3 are dimer + trimer ($BC + BC_2$ but not $B_2 + C_3$) and atom + tetramer ($B + BC_3$ but not $C + B_2C_2$).

Since $\rho(BC_2) \sim 5\rho(BC_3)$ in the initially deposited matrix, the $BC + BC_2$ source is dominant. Growth of B_2C_3 conclusively establishes the presence of BC in the matrix in an amount at least as great as the amount by which B_2C_3 grows.

Growth of BC_4 occurs primarily by $BC + C_3$ rather than $B + C_4$ or $C + BC_3$ because $\rho(C_3) \sim 10\rho(C_4)$ and $\rho(C_3) \sim 2\rho(BC_3)$. Growth of C_5 occurs by $C + C_4$ and $C_2 + C_3$, which establishes the presence of C and/or C_2 in the original matrix in an amount at least as great as C_5 growth.

Disappearance of triangular BC_2 requires breaking of one of its B-C bonds when one of its carbon atoms is attacked. The major reorganization of electronic energy involved in opening the ring appears to occur with little ($< \sim 3 \text{ kcal mol}^{-1}$) or no energy barrier, which makes this small molecule a candidate for an interesting *ab-initio* study of unusual reactivity at low temperature.

Conclusions

1. C_3 is linear but BC_2 , B_2C and B_3 are cyclic.
2. $n > 3$; $J = 0, 1, 2$ clusters are linear. Boron atoms cap the ends of linear chains.
3. $J = 0, 1, 2$ substitution in $n \geq 5$ clusters does not significantly affect IR intensities.
4. For $n \geq 5$ the absorption intensity of even n clusters is two to three times smaller than that of odd n clusters.
5. B_2C_2 grew most dramatically upon annealing. BC was not detected. Its upper limit column density is comparable to that of $n = 4$ clusters. B_2C_2 sources may be $2BC$ or $B + BC_2$ but $C + B_2C$ does not form B_2C_2 .
6. $n = 3, 4$; $J = 0, 1$ clusters disappear upon annealing but $J = 2$ clusters either grow or remain unchanged. Capping the ends of clusters with boron seems to render them inert to further condensation.
7. Statistical cluster distributions are apparent in $n = 4$ and 5 clusters. B_2C yields are too high and B_2C_{n-2} yields are too low in larger $n \geq 6$ clusters.
8. $n \geq 5$ clusters grow upon annealing and larger clusters grow more than smaller clusters.

Conclusions from Carbon HEDM Research

Quantitative analysis - Establishes HEDM density, distribution of carbon clusters, heat of formation of HEDM. Enables tracking of growth and decay of carbon clusters - carbon bookkeeping - quantification of "invisible carbon", C-atom and C_2 .

Highest density matrix (equivalent C-atom density ~ 1 mole percent in argon) contained 40% "invisible" carbon (C , C_2), determined by tracking the growth of the "visible" (measurable) carbon to a constant composition after repeated annealing. Main product of condensation is cyclic C_6 .

Yields of cyclic- C_6 are a factor of two larger than the combined yield of all other clusters in the fully condensed, highest density matrices. Cyclic- C_6 is the dominant condensation product.

Knudsen oven produces $\sim 80\%$ C_3 and $\sim 10\%$ each of C_2 and C-atom (by mass).

Laval oven with $\Delta T \sim 600$ K (between graphite surface and orifice) produces $\sim 5\%$ C_3 and C_2 and $\sim 90\%$ C-atom. C-atoms production by our oven (relative to C_3) is enhanced by higher temperature, which is accompanied by higher ΔT .

Substrate must be shielded from oven to prevent condensation during deposition.

Higher temperature oven places higher heat load on substrate, which promotes condensation.

Obtained higher density matrices by decreasing argon flux and maintaining oven flux. However, condensation was also increased.

One experiment with argon/5% H_2 caused nearly complete loss of C_{n+1} and C_{n+2} relative to C_{n+3} , suggesting that H_2 scavenges C-atoms efficiently during co-deposition.